Optical, thermal, strength properties and SHG efficiency of KDP single crystals doped with N,N'-dimethyl urea

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Pure single crystals of potassium dihydrogenphosphate (KDP) and the ones doped with N,N'-dimethylurea (NNDU) were grown by the temperature reduction method on a point seed. The dopant concentration in the mother liquor was 0.15 and 0.45 wt. %. The study of the transmission spectra of KDP-NNDU crystals, as well as the change in their strength properties (mechanical and laser strength) and thermal properties (differential thermal and thermogravimetric analyses) in the growth sectors (101) and (100) confirms the occurrence of NNDU molecules in both growth sector. It was shown that doping of the crystals with NNDU molecules led to an increase in the efficiency of second harmonic generation by two times in the sector (100) of KDP-NNDU crystals as compared with pure KDP.

Keywords: KDP crystals, N,N'-dimethylurea, laser damage threshold, microhardness, nonlinear optic materials.

Чисті і з доповненням N,N'-диметиломочевиною (NNDU') моноокристали дигідрофосфату калію (KDP) є одержано методом зниження температури на точковій затравці. Концентрація допута в маточному розчині складала 0,15 і 0,45 мас. %. Існує спектри пропускання кристалів KDP-NNDU, а також зміни їх міцності (механічна та лазерна міцність) і термічних (диференціально-термічний та термогравіметричний аналіз) властивостей у секторах росту (101) і (100), що підтверджує наявність молекул NNDU в обох секторах росту. Показано, що додавання кристалів KDP молекулами NNDU призвело до збільшення ефективності генерації другої гармонії у два рази у секторі (100) у порівнянні з чистим KDP.
1. Introduction

Well-known inorganic matrices, such as KDP (KH$_2$PO$_4$) group crystals with non-linear optical (NLO) properties, are often used to create new NLO materials by doping them with various organic and inorganic additives [1–4]. They continue to be popular as electro-optical materials (including those meant for production of optical elements) due to a relatively simple growth of crystals of required dimensions with good optical homogeneity. The use of KDP crystals in nonlinear optics is due to their high structural perfection, transparency in the UV region of the spectrum, and a relatively high threshold of laser destruction.

However, one of the main functional limitations of the use of KDP crystals in NLO applications is a relatively low value of the quadratic susceptibility (d$_{33}$ (KDP) = 0.38 pm/V [5]). There were introduced various additives the crystals in order to raise quadratic susceptibility of KDP, including molecules of organic compounds (Xylenol orange dye [1], amino acids [2–4, 6, 7]) and metal oxide nanoparticles [8, 9]. The introduction of amino acids into the crystal matrix led to an increase in the efficiency of second harmonic generation (SHG) by 1.75 times for KDP containing L-alanine [10], and by 1.14 times for KDP containing L-valine and L-threonine [3, 4], in comparison with that for the pure crystal. The doping of KDP with L-arginine amino acid led to the rise of NLO coefficients in comparison with that for the pure crystal by 1.33–1.74 times [2] and by 2.5 times in the case of KDP L-arginine crystals [6, 7]. The additives are found to influence the growth of the doped crystals and their physico-chemical characteristics.

The authors of [10] assumed that molecules of an organic additive could slightly distort KDP crystal lattice, thereby causing local deformations and polarization. Xue [11] shows the dominant contribution of PO$_4$ groups to the overall nonlinearity of KH$_2$PO$_4$ crystal. In addition, the increase in the SHG efficiency of doped KDP crystals may also be affected by the rise in the number of hydrogen bonds formed when some organic molecules are introduced into the crystal structure [12, 13]. It is known that hydrogen bond in some NLO inorganic crystals, such as HIO$_3$, NH$_4$H$_2$PO$_4$, KH$_2$PO$_4$, plays a very important role in the overall nonlinearity of the crystals. However, KDP crystals have only O–H···O type hydrogen bonds, while the crystals of NH$_4$H$_2$PO$_4$ group have two types of hydrogen bonds: O–H···O and N–H···O [13]. Both KDP and NH$_4$H$_2$PO$_4$ crystals have similar anionic structural units of H$_2$PO$_4^-$, but different cationic units (K$^+$ and NH$_4^+$). As reported in [13], in NH$_4$H$_2$PO$_4$ crystals the hydrogen bonds N–H···O make significant NLO contribution to the overall nonlinearity of the crystal (the coefficient d$_{33}$). In KDP-type crystals, despite the fact that the hydrogen bonds are disordered and centrosymmetric, they may contribute to the NLO properties such as quadratic electrooptical effect, nonlinear refractive index or harmonic generation [14].

In [15, 16] urea molecules were introduced into KDP crystals to increase the NLO properties. In this case, the amino groups present in urea structure replaced the potassium ions of KDP crystal matrix, which facilitated the entry of urea molecules into the crystal. In addition, urea molecules formed hydrogen bonds with the growing crystal faces. The introduction of additives into KDP crystals affects on the strength and other properties of the crystal matrix. As shown in [15], KDP:Urea crystals have higher mechanical properties than the pure crystals (~10 % at loads of 15–100 g in the sector {100}). The laser strength of KDP:Urea single crystals is increased by 20–25 % (when using YAG:Nd$^{3+}$ laser at 1.064 μm) compared to the one of the pure crystals [16]. The SHG efficiency of KDP:Urea single crystals increased approximately by 1.2 times as compared to that of pure KDP (for the crystals grown from the solutions containing 0.2–2 M Urea) [16].

It is known that 1,3-dimethyl urea (or N,N-dimethylurea, NNDU) urea derivative, has high NLO properties [17]. Moreover, NN/DMU molecules contribute to the increase in the NLO properties of L-arginine phosphate monohydrate [17] and KDP crystals [18]. The structure of NNDU molecules contains C=O group, which has acceptor properties and two N(CH$_3$)$_2$H groups, which have donor properties. The presence of H, O, and N atoms in the structure of NN/DMU may influence the formation of multiple hydrogen bonds between molecules and H$_2$PO$_4$ groups of KDP crystal, which leads to a modification of the properties of the crystal matrix [17]. Thus, it was of interest to grow a bulk KDP single crystal doped with NN/DMU molecules and investigate the effect of the
dopant on the change in the properties of KDP crystal.

In the present work we studied the influence of NN'DU molecules on the optical (linear and nonlinear) properties of KDP crystals grown from the solutions by the temperature lowering method. The influence of NN'DU molecules on the structural, strength (laser-induced damage threshold and micro-hardness) and thermal characteristics of doped KDP crystals was investigated.

2. Experimental

Pure and doped KDP single crystals were grown from aqueous solutions (pH 4.0±0.1) onto a point seed measuring 5×5×10 mm³ by the temperature lowering method in a 6.0 L crystallizer at a saturation temperature of 50°C. NN'DU (CH₃-NHCONHCH₃, pure ≥99 %, Aldrich) was used for doping KDP crystals at concentrations of 0.15 and 0.45 wt. % in the mother liquor (on the weight of KH₂PO₄ salt). The content of microimpurities (Fe, Al, Cr, Mg, Mn, etc.) in KH₂PO₄ salt was not higher than 10⁻⁵ wt. %.

The temperature was lowered at a rate of 0.3°C/day and 0.4°C/day for KDP and KDP:NN'DU crystals, respectively. The solution in the crystallizer was stirred at a speed of 70 rpm to provide dynamic growth conditions for the crystals. The crystals were grown dyring 1.5–2 months and had well-developed growth sectors {100} and {101} (Fig. 1). The average crystal growth rate was 1.4 and 1.0 mm/day for pure KDP, 1.3 and 0.6 mm/day for KDP:0.15 NN'DU and 1.3 and 1.2 mm/day KDP:0.45 NN'DU crystals. The samples measuring 10×10×10 mm³ with the sides parallel to the planes (100) and (001) were cut out from the crystal growth sectors {100} and {101} of the grown crystals for studies of their optical transmission, laser and mechanical strength. Then the samples were ground and polished.

The optical transmission of the crystals was studied in the spectral range of 200–1100 nm wavelengths using a Lambda 35 PerkinElmer spectrophotometer. The laser-induced damage threshold (LIDT) of the samples of KDP and KDP:NN'DU crystals was studied at the fundamental wavelength of YAG:Nd³⁺ laser operating at λ = 1.06 μm. During the measurements the energy of single-mode laser radiation pulse was 2.75 mJ, with 1 Hz the frequency of pulse repetition, the pulse duration τ = 10 ns, 1/e-radius of the focused spot being 45 μm. The focus of the optical system was located in the crystal bulk. The samples were irradiated by laser pulses at each point according to the scheme n−1–n (90 positions were irradiated 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 laser damage criterion was a spark of high-temperature glow visually observed at the crystal breakdown.

The Vicker's microhardness (HV) was investigated using a PMT-3 instrument in the load range of 10–200 g, as described in [6, 7]. The typical indenter descent rate was ~ 1 mm/min, each load being applied during 10 s. HV was calculated for each sample from the average of the results of 20 measurements on the planes (100) and (001) in the sectors {101} and {100}; the standard deviation did not exceed 2 %. The diagonal
prints were measured with an optical microscope ZEISS Axioskop 40. The microhardness value was calculated from the formula:

\[ H_V = 1.854P/d^2\text{(GPa)}, \]  

where \( H_V \) is the microhardness according to Vickers; \( P \), the applied load (N); \( d \), the average value of the measured lengths the diagonals (m).

Differential thermal (DTA) and thermogravimetric (TG) analyses of the crystals were realized on a MOM Q-1500D derivatograph (Hungary) in 20–550°C temperature range. The rate of heating was 2.5 deg/min; as a standard, there was used aluminum oxide. The samples of KDP and KDP:NN'DU crystals (\( \sim 1 \) g) for DTA and TG measurements were crushed in a corundum mortar.

The lattice parameters of KDP samples were measured on a general-purpose X-ray diffractometer using CuK\( \alpha \) radiation and graphite monochromator in a primary beam. Possible adjustment errors were minimized by means of the Bond method [19]. The rocking curves (RC) were obtained with double crystal spectrometer at CuK\( \alpha \) radiation with silicon monochromator adjusted to the (400) reflection. The used arrangement allows to pick out well-resolved K\( \alpha \) line of the X-ray spectrum. For the obtaining of RC’s in \((n, -m)\) scheme the (600) reflection of KDP samples was chosen, due to its Bragg reflection angle nearest to that of (400) Si. This considerably decreased the rocking curve broadening caused by dispersion. The measured values of Full Width at Half Maximum (FWHM) may be compared with the calculated ones obtained in accordance with [20, 21]. The diffraction line width \( \omega \) is given by the Darwin-Prins formula:

\[ \omega = 2r_0 \lambda^2 \pi V \frac{\mid F_{hh}\mid}{\sin 2\theta} \]  

Here, \( r_0 \) is the classical electron radius; \( \lambda \), the X-ray wavelength; \( V \), the volume of the unit cell; \( \theta \), the Bragg diffraction angle; \( F_{hh} \), the structure factor for specified reflection. Then, the angle spread:

\[ \Delta \theta = \frac{\Delta \lambda}{\lambda} \frac{1}{\cot \theta_M - \cot \theta_S}. \]  

Here, \( \theta_M \) and \( \theta_S \) are the diffraction angles of the monochromator and the sample, correspondingly. The spectral line width value \( \Delta \lambda = 0.000462 \) Å was adopted for CuK\( \alpha \) line [22]. Finally, FWHM:

\[ W = \sqrt{\omega_M^2 + \Delta \theta^2 + \omega_S^2}. \]  

Here, \( \omega_M \) and \( \omega_S \) are the diffraction line widths for the monochromator and the sample, correspondingly. The obtained value for the used arrangement is 7.2 arc. sec.

The NLO properties of the crystals were studied using YAG:Nd\(^3+\) laser at \( \lambda = 1.064 \) µm as described in [7] (with 1 Hz pulse frequency, 7 ns pulse duration, 1 mm laser beam diameter). The samples of pure and doped KDP crystals were cut out at the phase matching angle \( \theta = 59^\circ \) (Type II, \( o\omega e\)) from \{101\} and \{100\} growth sectors. The experiment was repeated for different input powers, and the corresponding output power was measured. The values of SHG efficiency were obtained from the ratio of the output to the input power.

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Fig. 2. UV-vis-NIR absorption spectra of KDP:NN’DU crystals for the sectors \{101\} (a) and \{100\} (b) with NN’DU concentrations: 0 wt. % (1), 0.15 wt. % (2) and 0.45 wt. % (3).
3. Results and discussion

KDP and KDP:NN'DU crystals were transparent and did not contain visible inclusions (Fig. 1). The introduction of NN'DU additives influenced the change of the crystal morphology. A slight blocking of the (100) faces of the growing crystal as compared to pure KDP crystal was observed at 0.15 wt. % NN'DU. The increase in the concentration of NN'DU to 0.45 wt. % also caused blocking of the (101) faces.

The transmission of KDP and KDP:NN'DU crystals in the visible region was ~ 87–90 % (Fig. 2). The decrease in the transmission of pure KDP crystal in 260–280 nm region for the sector {100} (curve 1, Fig. 2(a) as compared to that of the sector {101} (curve 1, Fig. 2(b) is due to the entry of the metal ions from the starting salt KH₂PO₄ into the sector {100} [23, 24]. As seen from Fig. 2, the absorption in the region of ~ 270 nm in KDP:NN'DU crystals exceeds the one in the pure KDP for both growth sectors. The increase in the concentration of NN'DU in the mother liquor from 0.15 to 0.45 wt. % leads to an increase in the absorption (decreasing the transmission) of the crystals in the ultraviolet region of the spectrum. This may be due to entry of NN'DU molecules into both crystal growth sectors. As shown in [16], the occurrence of Urea in KDP crystal increases with the rise of its concentration in the mother liquor.

The presence of the additive in KDP:NN'DU crystal also manifests itself during the measurements of its thermal characteristics. The DTA and TG curves of pure KDP and KDP:NN'DU crystals (the growth sectors {101} and {100}) are given in Fig. 3. A continuous 10–15 % loss of the mass of the samples studied is observed at temperatures up to 400 ºC. There are distinguished three sections on the TG curve in the temperature ranges of 20–220 ºC, 220–390 ºC and 390–550 ºC. The loss of the mass is insignificant for the first and the third sections due to removal of the adsorbed water (in the first section) and of the residual dehydration products (in the third section). The most intense loss is characteristic of the second section (13 %). Dehydration of KDP crystals is observed in the region of 200–380 ºC. On the DTA curve, we observe several exothermic peaks in the 210–380 ºC region, which correspond to dehydration of KDP crystals [25, 26]. The TG curves and peaks on the DTA curve practically coincide for pure KDP and KDP:NN'DU crystals. The decrease in the region of intense mass loss is observed for KDP:NN'DU crystals (intense mass loss ends at 395 ºC for nominally pure KDP, and at 370–380 ºC for the doped crystals). In addition, there is a significant redistribution of the DTA peaks. The redistribution of the intensity of the main DTA peaks at 260 and 275 ºC is due to evaporation of NN'DU (the boiling point of NNDU is 268–270 ºC). Therefore, the peak at 260 ºC becomes more intense for the doped crystals. In the high-temperature range (380–550 ºC), in contrast to nominally pure KDP crystal (for which the mass loss in this region is 0.4 %), the doped crystals show a mass loss of 1.8 % and 2.3 % in the growth sector {100} and {101}, respectively. Obviously, the process of NN'DU evaporation slows down removal of the residual dehydration products of KDP crystals. A more significant distinction for KDP:NN'DU in different growth sectors seems to be due to a greater binding force of NN'DU molecules entering into the sector {101}, in compar-
Table 1. Full Width at Half Maximum (FWHM) values measured in KDP crystals

<table>
<thead>
<tr>
<th>Sample</th>
<th>FWHM, arc. sec.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure KDP, (101), z</td>
<td>17.0</td>
</tr>
<tr>
<td>Pure KDP, (100), z</td>
<td>18.3</td>
</tr>
<tr>
<td>KDP:NN'DU, 0.45 wt. % NN'DU, (101), z</td>
<td>14.7</td>
</tr>
<tr>
<td>KDP:NN'DU, 0.45 wt. % NN'DU, (100), z</td>
<td>15.2</td>
</tr>
</tbody>
</table>

Table 2. Crystal lattice parameters of pure KDP and KDP:NN'DU (0.45 wt % NN'DU) crystals

<table>
<thead>
<tr>
<th>Crystals</th>
<th>c, Å</th>
<th>a, Å</th>
<th>Δc, Å</th>
<th>Δa, Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure KDP, (101)</td>
<td>6.9734</td>
<td>7.4528</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Pure KDP, (001)</td>
<td>6.9732</td>
<td>7.4526</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>KDP:NN'DU, (101)</td>
<td>6.9729</td>
<td>7.4522</td>
<td>–5·10⁻⁴</td>
<td>–6·10⁻⁴</td>
</tr>
<tr>
<td>KDP:NN'DU, (001)</td>
<td>6.9726</td>
<td>7.4527</td>
<td>–6·10⁻⁴</td>
<td>+1·10⁻⁴</td>
</tr>
</tbody>
</table>

son with the one of the molecules entering into the sector (101).

Incorporation of NN'DU molecules into KDP crystal may be due to the formation of hydrogen bonds between the oxygen and nitrogen atoms of NN'DU molecule and H₂PO₄ group on the (100) face of the growing KDP crystal. Moreover, it may be connected with the interaction between the oxygen atom from the group C=O of NN'DU molecules and the face (101) of KDP crystal with mainly positive charge [27–29].

To estimate the effect of NN'DU molecules on the structure perfection of the crystals there were measured the rocking curves and the crystal cell parameters a and c. The study of the rocking curves showed that the perfection of KDP:NN'DU crystals was extremely good, the crystals had no any internal structural grain boundaries and their perfection corresponded to that of pure KDP crystal (Table 1).

A significant decrease in the lattice parameters as against those of pure KDP (Δa = −5·10⁻⁴ Å and Δc = −6·10⁻⁴ Å) was observed for the samples cut out from the growth sectors (101) and (001) of KDP:NN'DU (0.45 wt. % NN'DU) (Table 2). It is known that KDP crystal has a tetramolecular unit cell with a = 7.452 Å and c = 6.974 Å [29]. In this case, a significant decrease in the lattice parameter a in the sector (101) (Δa = −6·10⁻⁴ Å) and its rise in (001) (Δa = +1·10⁻⁴ Å) in comparison with the one of pure KDP is observed for the doped crystal. Thus, KDP:NN'DU (0.45 wt. % of NN'DU) crystal is characterized by a "contraction" of the unit cell along the directions "c" ([001]) and "a" ([100]) in the sector (101), as well as along the direction "c" ([001]) and "stretching" along "a" ([100]) in the sector (001) in comparison with pure KDP. This leads to a decrease in the energy of the crystal lattice of KDP matrix due to rearrangements in the hydrogen bond system, and changes in the forces of electrostatic interaction between K–O ions.

Resistance to laser radiation is one of the main requirements for the crystals used for converting the frequency of laser radiation. The LIDT of KDP crystals is defined by optical breakdown on absorbing microinhomogeneities, and depends on the presence, nature and distribution of foreign inclusions and growth defects in the crystal.

The performed measurements show that the values of LIDT of both pure and doped...
Fig. 5. Microhardness as a function of loading for the sectors (101) (a) and (100) (b) of the plane (001): pure KDP (1), KDP: 0.15 wt. % NN'DU (2), KDP: 0.45 wt. % NN'DU (3).

Table 3. Microhardness of KDP and KDP:NN'DU crystals at indenter load \( P = 0.75 \) N

<table>
<thead>
<tr>
<th>NN'DU concentration in the mother liquor, wt. %</th>
<th>Sector (101)</th>
<th>Sector (100)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(001), GPa</td>
<td>(001), GPa</td>
</tr>
<tr>
<td>0</td>
<td>1.973</td>
<td>2.176</td>
</tr>
<tr>
<td>0.15</td>
<td>2.279</td>
<td>2.031</td>
</tr>
<tr>
<td>0.45</td>
<td>2.163</td>
<td>1.942</td>
</tr>
</tbody>
</table>

Table 4. SHG efficiency in KDP and KDP:NN'DU crystals at different NN'DU concentrations

<table>
<thead>
<tr>
<th>NN'DU concentration in the mother liquor, wt. %</th>
<th>Sector (101)</th>
<th>Sector (100)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>0.15</td>
<td>0.87</td>
<td>1.91</td>
</tr>
<tr>
<td>0.45</td>
<td>1.03</td>
<td>1.94</td>
</tr>
</tbody>
</table>

crystals are higher in [001] direction (compared with those in [100] direction) for the growth sectors {100} and {101} (Fig. 4). LIDT of KDP:NN'DU crystals decreases with respect to the one for pure KDP by 17–32 % for both growth sectors, the measurement error being 15 % (Fig. 4). However, in [16] it was shown that doping of KDP crystals by urea led to an increase in their LIDT by 20–25 %. The amino groups of urea molecules replace potassium ions in the crystal structure of KDP, causing hardening of the crystal. However, there is no amino group which could replace \( K^+ \) ions in the structure of NN'DU molecule. Probably, NN'DU molecules are embedded in the crystal between the growth layers, which results in distortion of the crystal lattice and affects its strength properties.

It is known that the laser strength of crystals is mainly correlated with their mechanical strength [30]. Taking into account the anisotropy of the mechanical properties of KDP crystal, the microhardness values were evaluated on two faces (001) and (100), and calculated from the formula (1). The results obtained with the optimum load on the indenter \( (P = 0.75 \) N) are presented in Table 3. Fig. 5 presents the loading curves of the growth sectors (101) (a) and (100) (b) on the face (001). The microhardness values obtained for the planes (001) and (100) of pure KDP crystal are similar to those already known [16]. The difference in the hardness of the faces (001) and (100) is due to their different crystallographic structure and to the fact that during their indentation different slip planes are activated [30].

The performed measurements showed that the doping of KDP:NN'DU crystal led to the rise of its hardening in the growth sec-
tor \(101\) by 15–20 \% (with a measurement error of 2 \%), and to softening in the sector \(100\) (Fig. 5, Table 3). The effect of NN'DU on the mechanical strength of the crystal may be due to changes in its structure and the interaction forces between the atoms [31], as well as to a decrease in the mobility of the point defects and the dopant molecules [32]. Different influence of NN'DU on the microhardness of \(101\) and \(100\) sectors of the KDP:NN'DU crystals is associated with different entering of the organic additive molecules into the growing faces, and with different nature of the interaction of the dislocations with NN'DU molecules in the \(101\) and \(100\) growth sectors.

The increase in the electrostatic attraction of K-O as a result of a decrease in the parameters \(c\) and \(a\) of the crystal cell of KDP:NN'DU may give rise to a smaller decrease of LiDT in the sector \(101\) (and also to an increase in mechanical strength) in comparison with LiDT (and mechanical strength) in the sector \(100\) of the doped crystal relative to pure KDP (Table 3).

The results of measuring the mediation conversion efficiency into the second harmonic of KDP and KDP:NN'DU crystals are presented in Table 4. It has been found that at NN'DU concentrations of 0.15 and 0.45 wt. \% the efficiency of SHG conversion of the doped crystals in the growth sector \(100\) increases approximately by two times as against the one of pure KDP. The values of SHG conversion efficiency are practically the same for the \(101\) growth sector of KDP:NN'DU crystals and pure KDP. These data correlate with the results obtained in [5]. In particular, when L-arg amino acid molecules were introduced into KDP crystal, there was observed the increase in SHG efficiency in the \(100\) sector by 3.9 times compared to the one of the pure crystals; for the \(101\) sector this efficiency increased by 2.5 times [5].

The increase of SHG efficiency in the \(100\) sector relative to that for the \(101\) sector in KDP:NN'DU crystal is probable due to both the entry of the molecules and the formation of additional hydrogen bonds between the molecules and the growing face of the crystal. It is known that the increase in the number of hydrogen bonds formed at the introduction of organic molecules into KDP crystals affects the efficiency of the SHG of the doped crystal [12, 13]. In addition, local distortion of the crystal matrix and emergence of the corresponding polarization [7] may result from the appearance of an organic molecule in the growing crystal, which increases SHG efficiency.

4. Conclusions

It was found that KDP crystals grown from a mother liquor containing NN'DU molecules (with concentration of 0.15 and 0.45 wt. \%) had a transmission of 87–90 \% in the visible spectral range and structural perfection. The presence of NN'DU molecules into both growth sectors (\(100\) and \(101\)) of KDP crystals was confirmed by optical spectroscopy method, X-ray, differential thermal and thermogravimetric analyses. It was shown that the efficiency of SHG conversion in KDP:NN'DU crystals for the sector \(100\) was higher by more than 2-time compared to the corresponding values of pure KDP. The introduction of NN'DU molecules into KDP crystal led to a decrease of LiDT in both growth sectors of the crystals; the microhardness in the sector \(101\) increased by 17–32 \%, but diminished in the sector \(100\).

References