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Structure perfection of large-size KDP crystals grown by various techniques

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The structure perfection of large-size KDP single crystals grown from nominally pure raw material by recirculation and solution temperature lowering techniques has been studied using the precision three-crystal X-ray diffractometry. The distribution inhomogeneity of the crystal lattice parameters $\Delta d/d$ over the grown crystal volume has been established. The crystals grown by the solution recirculation technique have shown an improved structure perfection.

Методами прецизионной трехкристальной рентгеновской дифрактометрии исследовано совершенство структуры крупногабаритных монокристаллов KDP, выращенных из номинально чистого сырья методами рециркуляции и снижения температуры раствора. Установлена неоднородность распределения параметров кристаллической решетки $\Delta d/d$ в объеме выращенных кристаллов. Более высокое совершенство структуры наблюдается для кристаллов, выращенных методом рециркуляции раствора.

The interest in water-soluble crystals (WSC) of the KDP (KH_2PO_4) group is due to numerous unique properties thereof. These properties, being combined with a high and rather reliable technological effectiveness of large-size pieces, provide a wide application field of KDP crystals in the modern laser engineering, as wide-aperture frequency multipliers and the Pockels cells [1]. The use of large-size pieces (40×40 cm^2 cross-section) in extra-high-power laser devices dictates high requirements to the crystals. Those include a high structure perfection, optical homogeneity, low absorption on the working wavelengths, high radiation resistance, and absence of various volume microdefects causing the front distortion of the passing wave and its scattering. The critical parameter for the high-power optical elements made from the KDP crystals is the damage threshold. It defines the size of the element withstanding high-power light loading without damage. Numerous experimental data on the laser damage of elements made of water-soluble crystals evidence that the damage is caused mainly by various structure defects arising during the crystal growing [1]. Today, the large-size KDP crystals capable of withstanding the light loading up to 30 J/cm^2 are grown by two techniques: the solution recirculation using a rectangular plate of the (001) orientation as a seed and the solution temperature lowering on a "point" seed with (100), (010), (001) facets [2].

The samples for X-ray studies of 2×2×2 cm^3 and 1×1×1 cm^3 size were cut out of KDP crystals grown at a rate of about 10 mm/day. Fig. 1 presents the crystal cut-out scheme. The cut samples were oriented in [100], [010], [001] directions to within ±0.2°. Then the facets were finished mechanically and the distorted near-surface layer was removed additionally using a cotton swab wetted in distilled water. Before, we have demonstrated the high efficiency of the three-crystal X-ray diffractometry (TXD) in the study of WSC structure perfection [1]. The latter is characterized

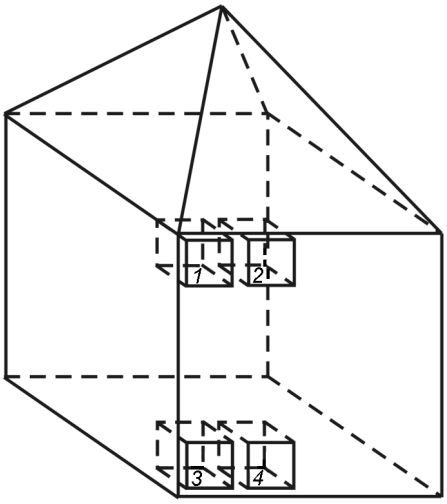

Fig. 1. Crystal cutout scheme.

rather comprehensively by certain parameters, namely, the diffraction reflection curve shape (DRC_S), the diffraction rocking curve (RC) halfwidth β, the integral reflection power I^R and the relative variation of the crystal lattice parameters $\Delta d/d$. The TXC methods provide the angular resolution of the (RC) peaks about 1 arcsec, the measurement errors of I^R and β about 2 % and the $\Delta d/d$ determination at an accuracy of $\pm 1 \cdot 10^{-7}$ [3]. The sample scanning at a pitch of 0.2 to 1.5 mm with respect to the incident X-ray beam provides the structure perfection characteristics for the whole surface under study. A specific feature of the TXD technique developed by the authors [4] consists in the arrangement scheme of the monochromators and the sample as well as the spacing thereof in the Bragg geometry (n, n, $-m$). This made it possible to minimize the spectral and angular dispersion and to obtain essentially "intrinsic" RCs for perfect crystals with the β value of about 6 arcsec even at different Bragg reflection angles for the second monochromator and the sample being studied.

Referring to the crystal cutout scheme of Fig. 1, studied were the samples cut out of two sectors of pyramid No.1, one sector of pyramid No.2 from the crystal upper part as well as Samples Nos. 3 and 4 from the lower part of the crystal grown by the recirculation technique. As to a crystal grown by the solution temperature lowering, the Samples Nos. 1 and 2 were cut out from two and one sectors of the pyramidal growth and the Samples Nos. 3 and 2, from two and one sectors of the prismatic growth, respectively. The scheme of the X-ray beam incidence on the surface being studied is shown in Fig. 2a, 2b, 2c. The samples were scanned at a pitch of 0.75 mm with respect to the incident X-ray beam and the parameters DRCS, $\bar{\beta}$, $\bar{I}^R$, (ratio of the experimental reflection power value to that calculated in the dynamic approximation) were measured in ten points of the sample. The values obtained were averaged; the results obtained are presented in Table 1.

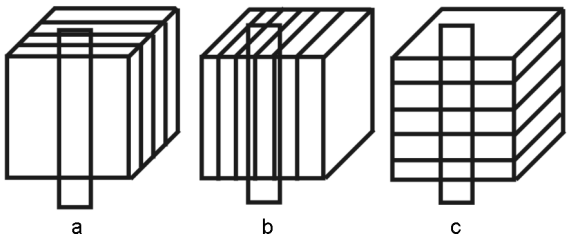

Fig. 2. X-ray beam incidence geometry.

The measurements were done using a TXD instrument in $CuK_{\alpha 1}$ radiation for (800), (080), (008) reflections at various positions of the growth layer stacks in the crystal with respect to the incident X-ray beam see Fig. 2). It is to note that at the crystal growth speeds of about 10 mm/day, the growth occurred in the kinetic mode according to the dislocation-layer growth mechanism [5]. The experimental data presented in Table 1 evidence a high structure perfection of the grown crystals at an insignificant perfection deterioration in the crystals grown by the temperature lowering technique. The experimental β and I^R values are comparable to the theoretical ones calculated under dynamic approximation and assumption of an ideal perfect crystal [6]. As a rule, the RC do not show any splitting that could be due to presence of angular misalignments of the growth layer stacks exceeding 1″. The angular misalignments seem to be so small (lower than the TXD method resolution threshold) that those do not result in any splitting and widening of the rocking curve at various sample positions with respect to the incident X-ray beam. The average values $\bar{\beta}$, $\bar{I}^R$ for (800), (080) reflections for the crystal grown by recirculation were 5.2″ and 3.57×10^{-6}; for the crystal grown by temperature lowering, $\underline{6}.1''$ and $3.80 \cdot 10^{-6}$; for the (00$\underline{8}$) reflection, $\beta = 5.8''$, $\bar{I}^R = 7.07 \cdot 10^{-6}$ and $\bar{\beta} = 7''$, $\bar{I}^R = 7.29 \cdot 10^{-6}$, respectively. It is to note that the concentration of structure defects is higher for the crystallographic plane (008) than that observed for the (800), (080) re-

Table 1. Structure characteristics of grown crystals.

Solution recirculation												
Sample	1			2			3			4		
Reflex parameters	$\bar{\beta}$, sec	$I^R_{ex}\cdot10^6$	I^R_{ex}/I^R_d	$\bar{\beta}$, sec	$I^R_{ex}\cdot10^6$	I^R_{ex}/I^R_d	$\bar{\beta}$, sec	$I^R_{ex}\cdot10^6$	I^R_{ex}/I^R_d	$\bar{\beta}$, sec	$I^R_{ex}\cdot10^6$	I^R_{ex}/I^R_d
(008)	7	7.18	2.36	6	7.15	2.42	6	7.02	2.36	6	7.18	2.37
$(008)_\perp$	6	7.02	2.41	5	7.02	2.38	5	7.02	2.36	5	7.04	2.36
(800)	5	3.38	1.15	5	3.97	1.35	5	3.43	1.16	5	3.80	1.33
$(800)_\perp$	5	3.41	1.16	5	3.7	1.25	5	3.38	1.15	5	3.70	1.30
(080)	6	3.64	1.23	5	3.64	1.23	6	3.67	1.24	6	3.69	1.25
$(080)_\perp$	6	3.61	1.22	5	3.12	1.06	5	3.80	1.29	5	3.22	1.20
Solution temperature lowering												
Sample	1			2			3			4		
Reflex parameters	$\bar{\beta}$, sec	$I^R_{ex}\cdot10^6$	I^R_{ex}/I^R_d	$\bar{\beta}$, sec	$I^R_{ex}\cdot10^6$	I^R_{ex}/I^R_d	$\bar{\beta}$, sec	$I^R_{ex}\cdot10^6$	I^R_{ex}/I^R_d	$\bar{\beta}$, sec	$I^R_{ex}\cdot10^6$	I^R_{ex}/I^R_d
(008)	7.1	7.37	2.47	6.6	7.11	2.39	7.2	7.35	2.47	7	7.41	2.49
$(008)_\perp$	6.9	7.27	2.44	6.8	7.31	2.45	7.1	7.17	2.41	7	7.31	2.45
(800)	5.8	3.70	1.25	6.4	3.74	1.27	5.9	3.74	1.27	6.1	3.73	1.26
$(800)_\perp$	5.8	3.76	1.27	5.9	3.78	1.28	6.1	3.73	1.26	6.3	3.73	1.26
(080)	6.4	3.88	1.32	5.6	3.79	1.28	6.8	4.41	1.49	6	3.76	1.27
$(080)_\perp$	6.4	3.76	1.27	6.3	3.71	1.26	6	3.70	1.25	6.3	3.76	1.27

flections in all the samples studied. This is associated with the presence of growth layers that are more pronounced both at pyramidal and prismatic crystal growth.

The crystals under study were grown from high-purity raw material (according to production technology from the Institute for Single crystals) that guarantees the limiting impurity concentration at a level of 10^{-5} to 10^{-6} wt. %. However, even when that raw material is used, the solution contains substantial amounts (about 10^{-3} to 10^{-4} wt. %) of individual impurities (Na, Si, As, Rb) as well as structure units of organic compounds different from those included in the KDP crystal lattice; those impurities could cause inhomogeneities in the grown crystal volume and changes in the crystal lattice parameters [1, 7]. We have measured the crystal lattice parameters d and $\Delta d/d$ variations over the crystal volume at high accuracy using the method [3]. As a reference, the Sample No.2 was taken from the crystal grown by the solution recirculation, the geometry was according to Fig. 2a. Onto that reference, the samples being studied were placed in positions a, b, and c with respect to the X-ray beam hitting simultaneously the sample and the reference. The sample under study was turned with respect to the reference at an angle ε exceeding the rocking curve halfwidth. The rocking curves were recorded simultaneously for (200), (400), (600), (800) reflections as well as for (020), (040), (060), (080) ones, thus making it possible to determine the $\Delta\Theta_{hkl}(\mathrm{tg}\Theta_{hkl})$ dependence, to determine the turn angle ε of the sample reflecting plane, and to calculate $\Delta d/d = -\mathrm{tg}(\Theta_{hkl} - \varepsilon)\mathrm{ctg}\Theta_{hkl}$, as well as $d_{sam} = d_{ref} \pm \Delta d/d$.

The $\Delta d/d$ determination procedure made it possible to minimize the effect of corrections associated with the X-ray refractive index, thermal expansion coefficient α_i and other dispersion corrections [3]. For example, α_i for KDP crystals is about $3.43\cdot10^{-5}$ deg^{-1}. This technique provides additional information on the lattice period gradient over the depth of the near-surface crystal layer. Fig. 3 shows a typical $\Delta\Theta_{hkl}(\mathrm{tg}\Theta_{hkl})$ dependence for a sample (No.1 in Fig. 2a geometry) grown by recirculation. The linear dependence evidences the absence of the lattice period gradient over the X-ray beam penetration depth into the crystal. The straight line slope with respect to the abscissa axis defines the difference between the lattice periods of the sample and reference. For the (800) reflection having $\Theta \sim 55.8°$, the $\Delta d/d$ error is $\pm2.5\cdot10^{-6}$ at the $\Delta\Theta = \pm0.5°$. The measurement results of

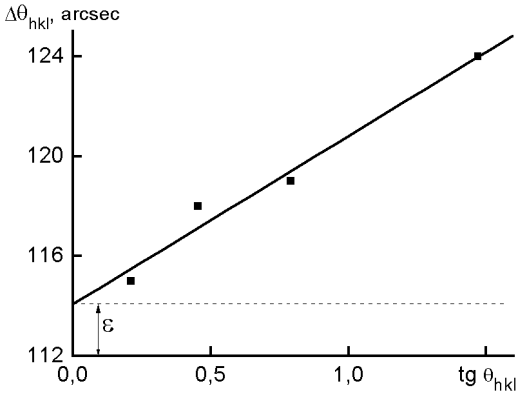

Fig. 3. $\Delta\Theta_{hkl}(\mathrm{tg}\Theta_{hkl})$ dependence character for (200), (400), (600), (800) reflections.

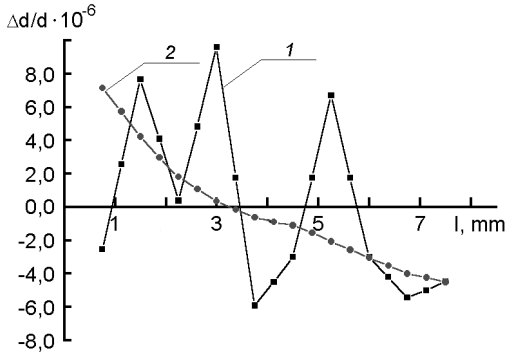

Fig. 4. $\Delta d/d(l)$ variation character for Sample No.3 grown by temperature lowering, the sample in position *b* (*1*) and *c* (*2*).

$\Delta d/d$, lattice parameters *a* and *b* and $\Delta = b - a$ are summarized in Table 2. An inhomogeneity in parameters $\Delta d/d$, *a*, *b*, and Δ over the crystal volume has been revealed, especially in the crystal areas grown at one pyramid facet (Samples 2, 4) and at two pyramid facets (Samples 1, 3) by recirculation and at prismatic facet growth (Samples 3, 4) by the solution temperature lowering.

Such an essential inhomogeneity in $\Delta d/d$ and lattice parameters is connected first of all with the specific feature of the WSC growth mechanisms. Those include the supersaturation fluctuations at the crystallization front during the growth resulting in an inhomogeneous distribution of some impurities and the inclusion thereof into the crystal lattice, as well as the structure defects in the crystal volume. The crystal grown by the temperature lowering technique exhibits increased differences in $\Delta d/d$ and the lattice parameters. The previous studies using optical polarization [8, 9] evidenced inhomogeneities in anomalous biaxiality 2V and γ (the slope angle of optical axes) over the crystal volume. It is to note that the anomalous biaxiality of KDP crystals is the main factor defining the transmission contrast of electrooptical modulators made therefrom [10]. Numerous researchers [1, 8, 9] ascribe the anomalous biaxiality to the residual internal stresses in the crystal. Those assumptions are confirmed by X-ray measurements of $\Delta d/d$ over the crystal volume (Table 2). The scanning (at 0.375 mm pitch) of Sample No.3 (grown by temperature lowering) in the position of Fig. 2b have demonstrated the $\Delta d/d$ variation character ($\Delta d/d = \Delta\overline{d}/d - \Delta d/d_i$) over the sample cross-section (Fig. 4, curve *1*) and the $\Delta d/d$ variation character in Sample No.3 in in the position of Fig. 2c (Fig. 4, curve *2*). The $\Delta d/d(L)$ variation character (Fig. 4, curve *1*) evidences an inhomogeneous impurity distribution over the growing crystal volume and is connected, first of all, with the dislocation-layered mechanism of the crystal growth. As the sample is turned at 90° (see Fig. 2c) where the averaged values are measured over the growth layer stacks, a monotonous decrease of $\Delta d/d$ is observed from the crystal central part to its periphery (see Fig. 4, curve *2*). The integral reflection values I^R of the X-ray beam were

Table 2

Growth method	Solution recirculation				Solution temperature lowering			
	$\Delta d/d \cdot 10^5$				$\Delta d/d \cdot 10^5$			
Sample	1	2	3	4	1	2	3	4
(080)	+2.47	+3.7	+5.82	+2.91	+5.09	+1.25	+7.19	+4.36
(800)	−3,43	−7	−12.3	−7.27	−11.39	−13.23	−11.22	−18.42
a, Å	7,45083	7,45099	7,45004	7,45053	7,45019	7,45004	7,45070	7,44963
b, Å	7.45122	7.45110	7.45149	7.45126	7.45122	7.45112	7.45160	7.45137
$\Delta = (b - a)\cdot 10^4$, Å	3.9	1.1	14.5	7.3	10.3	10.8	9	17.4

measured for the same sample positions and in the same points (Fig. 5). The $I^R(l)$ variation character shows the concentration distribution of the structure defects (dislocations, conjugation boundaries of the growth layers, etc.) over the sample cross-section (Fig. 5, curve *1*). In the sample position of Fig. 2c, a monotonous decrease of $I^R(l)$ is observed (Fig. 5, curve *2*) that characterizes the structure perfection and its variation over the sample cross-section. The presence of growth layer stacks, even at insignificant set of $\pm\Delta d/d$ values, results in an additional RC widening and increased integral reflection power.

Although the studied KDP crystals show a rather high radiation resistance (20 to 30 J/cm^2 at $\lambda = 1.064$ μm at $\tau = 10$ ns), the precision three-crystal X-ray diffractometry evidences the variation of $\Delta d/d$ over the crystal volume. The largest variations are at the conjugation areas of the prismatic and pyramidal growth facets. The anomalous biaxiality measured previously as 2V by optical polarization techniques as well as the direct X-ray techniques have confirmed the biaxiality cause as that connected with the residual stresses in the crystal. The values and distribution character of $\Delta d/d$ and 2V over the crystal volume are in a good correlation. The rocking curve half-width β and integral X-ray beam reflection power I^R evidence a rather high structure perfection and distribution homogeneity over the crystal volume.

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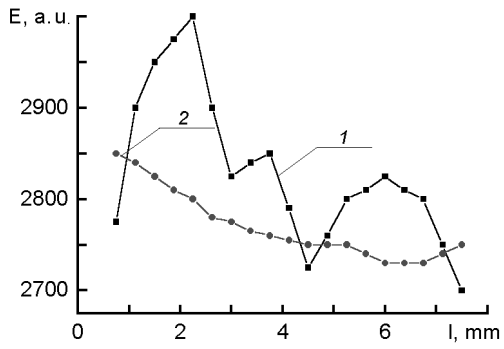

Fig. 5. Variation character of integral reflection power for Sample No.3 grown by temperature lowering, the sample in position *b* (*1*) and *c* (*2*).

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Досконалість структури великогабаритних кристалів KDP, вирощених різними методами

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Методами прецизійної трьохкристальної рентгенівської дифрактометрії досліджено досконалість структури великогабаритних монокристалів KDP, вирощених із номінально чистої сировини методами рециркуляції та зниження температури розчину. Встановлено неоднорідність розподілення параметрів кристалічної гратки $\Delta d/d$ в об'ємі вирощених кристалів. Більш висока досконалість структури спостерігається для кристалів, вирощених методом рециркуляції розчину.