

Study of structure perfection of KDP single crystals using the X-ray dynamic diffraction effects

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In potassium dihydrophosphate single crystals grown from aqueous solutions using the temperature lowering technique, the anomalous X-ray transmission (Borrmann effect) has been shown in experiment. The dependences of integral intensity of anomalously transmitted beam (T_i) and Laue reflected (R_i) one on the thickness t of the sample being studied have been found; these dependences made it possible to determine the dynamic approximation region for a "thick" crystal. Fot that region, the integral coefficients of dynamic absorption μ_i and integral characteristic y_i have been determined under dynamic approximation. The high sensitivity of the μ_i parameter to the presence of coherent conjugation boundaries between the packages of growth layers is demonstrated.

На монокристаллах дигидрофосфата калия, выращенных из водных растворов методом снижения температуры, экспериментально показано наличие аномального прохождения рентгеновских лучей (эффект Бормана). Получены зависимости интегральной интенсивности аномально прошедшего T_i и Лауэ отраженного R_i пучков от толщины исследуемого образца t, которые позволили определить область динамического приближения для "толстого" кристалла. Для этой области в динамическом приближении определены и вычислены интегральные коэффициенты интерференционного поглощения μ_i и интегральная характеристика y_i. Показана высокая чувствительность параметра μ_i к наличию в кристаллах когерентных границ сопряжения между пакетами слоев роста.

1. Introduction

The KDP single crystals are among materials for different elements of power optics, quantum electronics, and laser engineering due to the unique properties thereof: high radiation resistance againts laser radiation, high optical and structural homogeneity, and well developed techniques for growing large-size (600×600×1000 mm^3) [1]. The laser destruction threshold for optical elements made of KDP crystals is the critical parameter that defines the size of an element able to withstand the high-power light loadings without damage. Experimental results obtained in studies of KDP crystal laser-induced damage evidence that the main factor defining the laser damage resistance is the presence of structure defects in the grown crystal. Those defects include: the conjugation boundaries between prismatic and pyramidal growth segments, the mother liquor inclusions as well as different introduced impurities in the crystal volume and the distribution character thereof.

When studying the crystal structure perfection of KDP crystals, the high-resolution X-ray and optical examination methods turned out to be of high efficiency. The study of laser damage resistance of KDP samples have shown its difference by several times over the sample volume, while the X-ray and other study methods did not shown any substantial structure imperfections. The use of X-ray methods based on dynamic diffraction of X-rays in perfect crystals and, in particular, the anomalous X-ray transmission effect (Borrmann effect) [2, 3]. Experimental works [4–7] confirm the influence of even insubstantial periodicity disturbances in the crystal lattice on the anomalous transmission effect. The studies were carried out as a rule using two-crystal diffractometers with monochromator and the sample under study being arranged in the $(n, -n)$ scheme on Ge, Si crystals having a hich reflectivity. In [6], it was found theoretically and in experiment that to reveal the slightest disturbances in the crystal lattice, the optimum is the use of the dynamic approximation region of a "thick" crystal when only one wave field attains the surface of the sample under study. It was shown [6] that in this region, the linear dependence $\ln i = -\mu_i t + y_i$ is valid, where $i = T_i = R_i$, T_i, R_i are integral reflection powers of the anomalously transmitted and Laue reflected beam; t, the sample thickness; μ_i, the integral interference absorption coefficient; y_i, the integral chatacteristic equal to the intercept of the continued straight line on the ordinate axis. The characteristics μ_i and y_i will be used in what follows to study the effects of different disturbances in KDP crystals at the anomalous X-ray transmission.

2. Experimental

The KDP crystals were studied grown from aqueous solutions by temperature lowering on a point seed with face orientations (100), (010) and (001) — x, y, z cuts with a deviation from the sample surface crystallographic orientation $\Delta\theta \leq 0.5°$. The samples were finished by a standard technique [1] and then thinned by dissolution in distilled water at room temperature. The samples were cut out of both prismatic and pyramidal crystal segments. The presence of the layer-by-layer growth in the samples defined two types of arrangement thereof relative to the incident X-ray beam (parallel and perpendicular). For different thickness and arrangements of the layer-by-layer growth boundaries relative to the incident X-ray beam, the following characteristics were recorded: rocking curves in the Bragg geometry, in the Laue geometry for reflection, and the transmission with recording of the diffraction reflection curves (DRC), fixation of the integral reflection intensity E (pulses) and the angular positions of the diffraction bands. Those experimental results made it possible to determine the structure-sensitive parameters such as the angle of turn between the growth layer packages, α, the coherent section of the growth layer packages, l, and the distribution thereof in the sample, the rocking curve full width at half maximum (FWHM), β, in arcses, the integral reflection power, I^R, in the Bragg geometry, and the integral reflection power, R_i, and the transmission one, T_i, in the Laue geometry, for different sample thickness values. Experimental measurements were carried out using a triple-crystal X-ray diffractometer (TXD) [9] in $CuK_{\alpha 1}$ emission. In TXD, the monochromator crystals and the crystal under study were arranged in the $(n_1, n_2, -m)$ scheme, which, according to [8], made it possible to minimize the contributions from the wave and angular dispersion and to obtain the experimental DRC close to theoretical ones in the approximation of the dynamic theory of X-ray diffraction in perfect crystals. As the monochromators (n_1 and n_2), Ge single crystals with dislocation density $\rho \leq 10^2$ cm^{-2} were used. The Bragg reflection angle for these crystals was $\theta \sim 45°$. The instability of the recording scheme and of the primary X-ray beam intensity did not exceed ± 0.5 %. The integral reflection power of DRC was determined to within $\leq \pm 1$ %. The incident beam width was 50 μm at 8 or 12 mm height. The incident X-ray beam intensity $I_0 = 2500-7000$ pulses per second, depending on X-ray tube voltage and current and the beam height. Such intensity range provided a reliable DRC recording by a curve-tracer at the sample rotation at a rate of 0.01–0.005 deg/min near the Bragg reflection angle, the open slit counter being fixed in the 2Θ position. The background intensity at the DRC tails was ≤ 1 pulse/s in reflection geometries and ~2 pulse/s in transmission ones and was taken into account when determining the integral reflection intensity E (pulses) from the specified reflection. The measurements were made using the KDP samples of differing in thickness (one and the same sample was thinned by polishing). The studied thickness range was $0.06 \leq t \leq 0.2$ cm, thus corresponding to μt variation range $8.76 \leq \mu t \leq 25.00$.

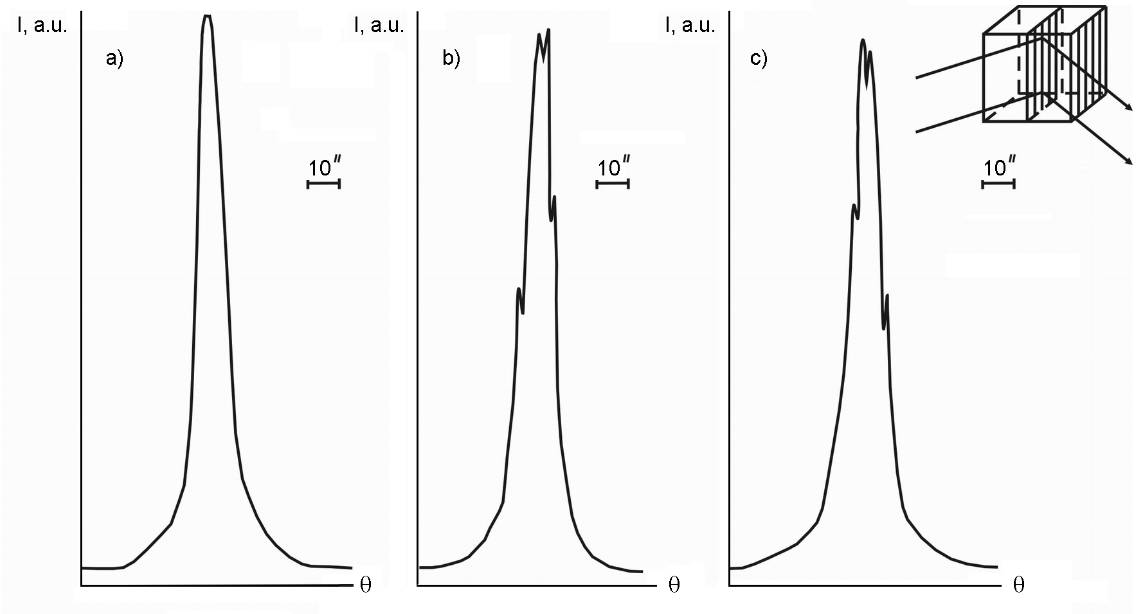

Fig. 1. Typical rocking curves for (200) reflection recorded in different geometries. The position of the growth layer packages relatively to the incident beam is shown schematically (a, the Bragg geometry; b, the Laue geometry for reflection; c, as b for transmission).

3. Results and discussion

The calculated coefficient of normal photoelectric absorption for KDP amounts $\mu = 143.64$ cm^{-1}. The mass absorption coefficients μ/ρ for K, H, P, O were calculated using the data taken from table [10] with correction for $CuK_{\alpha 1}$ ($\lambda = 1.54051$ Å) emission, since in [10] the μ/ρ values are presented for $\lambda = 1.542$ Å. The experimental values of the integral power $\overline{T}_i$ and $\overline{R}_i$ and the rocking curve (FWHM) β_{T_i}, β_{R_i} of the (200) reflection for different thickness t of the sample studied as well the values of $\overline{\beta}^R_{800}$, $\beta^{I^R}_{800}$ (arcsec) in the Bragg reflection geometry for (800) reflection are presented in the Table (all the values are averaged from 5 measurements).

It is seen from the Table that for $24.99 \geq \mu t \geq 15.37$ $T_i = R_i = i$, the rocking curve (FWHM) and is about 5.1 arcsec. In the Bragg geometry, $\beta_{200} \approx 9$ arcsec, that is due to the presence of distorted near-surface layer in the samples as well as to complex physical interactions between the incident and reflected X-ray beam at changing penetration depth near the Bragg reflection angle [11]. Fig. 1 (a, b, c) shows the DRC for a $t = 0.169$ cm sample with parallel arrangement of the X-ray beam relative to the semicoherent boundaries of the layer-by-

Table. Crystal structure characteristics

t, mm	1.74	1.69	1.29	1.25	1.07	0.85	0.71	0.61
μt	24.99	24.28	18.53	17.96	15.37	12.21	10.20	8.76
$\overline{R}_i \cdot 10^6$	0.134	0.140	0.345	0.387	0.531	0.860	1.160	1.0
$\overline{T}_i \cdot 10^6$	0.136	0.152	0366	0.446	0.570	1.03	1.54	1.97
$\overline{T}_i/\overline{R}_i$	1.09	1.01	1.06	1.15	1.07	1.20	1.33	1.41
$\overline{\beta}_{R_i}$, arcsec	5.1	5.1	5.0	5.1	5.1	5.6	5.8	6.0
$\overline{\beta}_{T_i}$, arcsec	5.1	5.1	5.1	5.0	5.1	5.6	5.8	6.0
$\overline{I}^R_{800} \cdot 10^5$	3.70	3.71	3.70	3.71	3.72	3.74	3.74	3.75
$\overline{\beta}^{I^R}_{800}$, arcsec	6.4	6.3	6.3	6.4	6.2	6.4	6.5	6.6

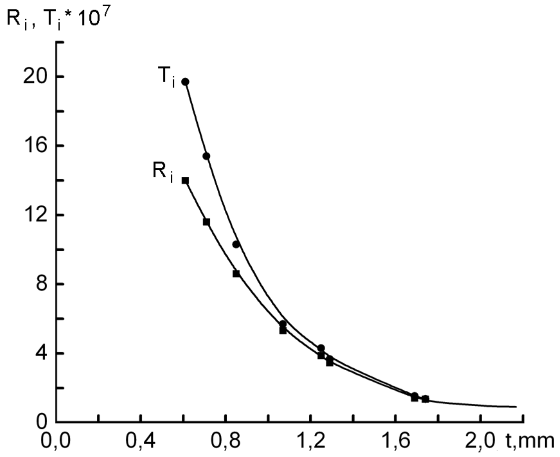

Fig. 2. Dependences of integral intensity of the Laue reflected ($\overline{R}_i$) and Borrmann transmitted ($\overline{T}_i$) X-ray beams on the sample thickness (t).

layer growth imaged in the Bragg geometry for reflection and in the Bragg-Laue one for transmission, R_i, T_i. As is seen in Fig. 1 (b, c), the DRC taken in the Bragg geometry for reflection and in the Bragg-Laue one for transmission, R_i, T_i, provide a higher angular resolution. The DRC splitting for T_i and R_i reflections is due to the presence of semicoherent boundaries between the growth layer packages having angular turn about 1 to 3 arcsec. The diffraction contrast from two growth layer conjugation as well as between between the growth layer packages having angular turn exceeding 10 arcsec was observed before in [12]. The experimental rocking curves (Fig. 1b, c) confirm the identity of DRC (FWHM) $\beta_{T_i} = \beta_{R_i} =$ 5.1 arcsec for T_i and R_i beams as well as the DRC split into four peaks. Since the dislocation density in the crystals under study is $\rho \leq 10^2$ cm^{-2}, thus exluding completely the low-angle ordered dislocation boundaries, the DRC split is due to semicoherent boundaries between the growth layer packages only. Taking into account the cross-section of the X-ray beam incident the sample (the Bragg-Laue geometry, reflection (200)) about 51 μm and the presence of four peaks in DRC, the growth layer package width is easy to estimate bearing in mind that the line intensities in maximum is in proportion with the growth layer package width that is 8, 11, 16, 16 μm. Since in the Bragg-Laue geometry the DRC are taken from the whole sample thickness, those characterize the crystal structure perfection

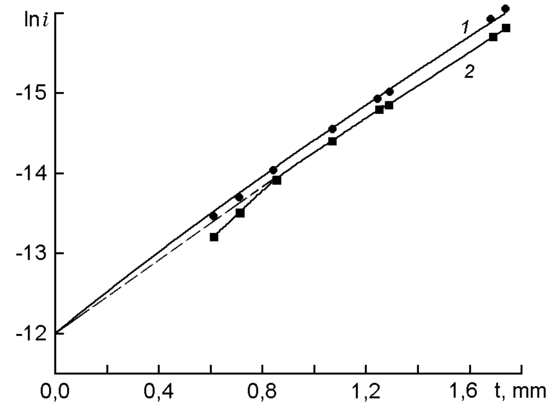

Fig. 3. Dependence of ln$i$ on the sample thickness with notation of the growth layer packages position: (*1*), parallel and (*2*), perpendicular to the incident X-ray beam. $i = T_i = R_i$.

in a more correct fashion than the Bragg geometry. The above makes it possible to provide an unique technique for nondestructive study of the sample structure perfection using the scanning in relation to the incident X-ray beam.

The dependences of the integral reflection power T_i and R_i on the sample thickness taken for KDP with $\rho \leq 10^2$ cm^{-2}, reflection (200) are presented in Fig. 2. It is seen that for thickness $t \leq 1.07$ mm, functions $T_i = f_1(t)$, $R_i = f_2(t)$ are deviated from linearity and the reflection energy is redistributed relatively between T_i and R_i ($T_i \geq R_i$). This is due to appearance of two wave fields at the surface of the X-ray beam exit [6]. At the thickness $t \leq 1.07$ nm with $\mu t \leq 15.37$, there is the "thin" crystal approximation region with a sharply increasing $T_i = f_1(t)$ section. A more correct definition [6] of the dynamic approximation interval for a "thin", "intermediate", "thick" crystal follows from the logarithmical dependence $\ln T_i(t)$, $\ln R_i(t)$, presented in Fig. 3. Theoretical calculations and experimental results obtained in [6] have confirmed that in the dynamic approximation of the "thick" crystal region where $T_i = R_i$ i $= i$, the $\ln i = -\mu t + y_i$ is linear. The experimental curve for KDP crystals (Fig. 3) confirms that fact and makes it possible to determine the parameters μ_i and y_i proceeding from $\mathrm{tg}\alpha = \Delta\ln(i)/\Delta t = -\mu_i$. The parameter μ_i can be considrered as a certain effective absorption coefficient that characterizes the $12.21 \leq \mu t \leq 24.99$ region of the "thick" crystal dynamic approximation where $T_i = R_i = i$. Therefore, it is reasonable to introduce for the region $\mu t \geq 12.21$ the concept of the integral coefficient of the interference absorption $\mu_i = 21.00$ cm^{-1} that is very sensitive to insignificant disturbances of the crystal lattice [6].

For KDP single crystals, the linear coefficient of normal photoelectric absorption $\mu = 143.64$ cm^{-1} and the ratio $\mu_i/\mu = 0.146$, thus, μ_i is less than μ by a factor of 6.840. Since the continuation of the experimental curve $\ln i = f(t)$ intersects the ordinate axis not at zero (Fig. 3), it is logical to introduce the second integral charactertistic $y_i = -11.9$ equal to the intercept at the ordinate axis. In general, μ_i and y_i are to be considered as quantitative characteristics of the anomalous X-ray transmission through a KDP crystal being in the Laue position in the case of dynamic approximation of a "thick" crystal. The changes in μ_i and y_i depending on one or other defect kind in the crystal may be considered as the general characteristic of the crystal lattice. For the first time, it has been found in experiment that one kind of the crystal lattice distortions in the samples studied is the presence of semicoherent boundaries between the growth layer packages being clearly recorded in the DRC taken in Laue geometry for reflection R_i and for transmission T_i, Fig. 1b, c. To clear up the effect of those boundaries on anomalous X-ray beam transmission, the sample being studied was arranged with parallel and permendicular position of the boundary relatively to the incidens beam streak. The depencences of the integral reflection power for the transmitted T_i and reflected R_i beams for different thickness t and positions of the sample, Fig. 3.

From the $\ln i(t)$ dependence, the integral coefficient of the interference absorption μ_i and y_i were determined. For parallel arrangement of semicoherent boundaries relative to the X-ray beam streak (Fig. 3, curve *2*), $\mu'' = 22.25$ cm^{-1}, for perpendicular one, $\mu' = 21.00$ cm^{-1}, $y_i = -11.9$ being unchanged. The "thick" crystal dynamic approximation for KDP crystals and $CuK_{\alpha 1}$ emission is $15.2 \leq \mu t \leq 28.73$. The sensitivity of the anomalous X-ray beam transmission to the crystal lattice disturbances increases as the sample thickness rises, although some difficulties appear in the low intensity recording. It is to note that the observation in the Bragg-Laue geometry provides information from the whole sample volume with insignificant contribution from two near-surface layers. This fact manifests itself in an enhanced angular resolution of DRC, new quantitative μ_i and y_i parameters characterizing the structure perfection of the crystals studied.

4. Conclusion

Thus, in spite of low reflectance of X-rays and the complex crystal lattice consisting of four elements, the Borrmann effect has been revealed in KDP crystals in experiment for the first time. The further use and development of the method will make it possible to characterize more completely the structure perfection of the single crystals being grown, while the experimental data obtained in combination with results of other analytical methods will provide a judgement on the effect of different defects on the functional properties of the material.

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Дослідження досконалості структури монокристалів KDP з використанням ефектів рентгенівської динамічної дифракції

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На монокристалах дигідрофосфату калію, вирощених з водних розчинів методом зниження температури, експериментально показано наявність аномального проходження рентгенівських променів (ефект Бормана). Одержано залежності інтегральної інтенсивності аномально пропущеного T_i та Лауе відбитого R_i пучків від товщини зразка t, що досліджено, які дозволили визначити область динамічного наближення для "товстого" кристала. Для цієї області у динамічному наближенні визначено та обчислено інтегральні коефіцієнти інтерференційного поглинання μ_i та інтегральну характеристику y_i. Показано високу чутливість параметра μ_i до наявності у кристалах когерентних меж сполучення між пакетами шарів росту.