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Variation of crystal lattice parameters of KDP single crystals containing impurities

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KDP single crystals grown from aqueous solutions by the recirculation method from nominally "pure" raw material and added impurities Ca, Si, Pb, Cr, hydrogen peroxide were studied by high resolution X-ray method. It was found that additional introduction of impurities leads to a deterioration of structural quality of crystals. The main growth defects of crystals at dislocation density ~ 10^2 cm^{-2} at the absence of zonarity and sectoriality is the impurity striation and presence of low-angle quasi-boundaries. A correlation between the concentration of low-angle quasi-boundaries, dispersion of structure-sensitive parameters and the bulk laser damage resistance of crystals is observed.

Кристаллы KDP, выращенные из водных растворов циркуляционным методом из номинально "чистого" сырья и сырья с добавками Ca, Si, Pb, Cr и перекиси водорода, исследованы методом рентгеновской дифрактометрии высокого разрешения. Показано, что дополнительное введение примесей приводит к ухудшению структурного совершенства кристаллов. Основными дефектами роста кристаллов при плотности дислокаций ~10^2 $см^{-2}$ и при отсутствии зонарности и секториальности являются примесная полосчатость и наличие малоугловых квазиграниц. Наблюдается корреляция между концентрацией малоугловых границ, дисперсией структурно-чувствительных параметров и величиной объемной лазерной прочности кристаллов.

The character of entry and distribution of impurities in the volume of KDP crystals defines to a large extent the structural perfection, optical homogeneity and, consequently, functional parameters of articles made of those crystals. The concentration and distribution character of homogeneously and heterogeneously trapped impurities by the growing crystal is only very rarely homogeneous over the crystal volume. The main sources of impurities that enter the growing crystal are those present in the raw material, water, and the crystallizer material. In order to control the growth parameters and the crystal properties, ions of polyvalent metals are purposefully added very often to the solution [1]. A thorough purity degree analysis (including 37 impurity elements) of the used raw material for the KDP crystal growth (carried out at the leading companies in the world) presented in [2] has shown that the total content of the controlled impurities even in the "best" raw material is over $1.2 \cdot 10^{-4}$ wt %. A multiform and often uncontrolled entry and distribution character of impurities in the growing crystal volume requires further works on raw material purification, control improvement of the growth parameters and development of informative quantitative study methods making it possible to determine the effect of the impurities on structural quality and laser radiation resistance of KDP crystals.

KDP single crystals, 400×400 mm^2 in cross-section, were grown by solvent recirculation method from aqueous solutions at 80°C on prismatic seeds at a rate of 1 mm/day along the direction [001]. The growing was carried out by one and the

Table 1. The averaged values β, I^R, σ for different reflections {hkl}

N	Sample	{hkl}	β, arcsec	σ_β	I^R, 10^6 rad	σ^R	P, J/cm^2
1	KDP(2)	(800)	7.20	0.58	1.49	0.12	70.0
		(008)	7.69	0.28	8.89	0.19	
		(206)	6.53	0.66	1.59	0.19	
2	KDP(Ca)	(800)	10.10	1.24	1.97	0.34	10.0
		(008)	9.80	0.87	11.60	0.35	
		(206)	8.70	1.25	2.46	0.69	
3	KDP(Si)	(800)	7.99	0.99	1.56	0.27	14.0
		(008)	7.94	0.71	9.41	0.28	
		(206)	6.82	0.97	1.92	0.54	
4	KDP(Pb)	(800)	7.94	0.98	1.55	0.26	20.0
		(008)	7.85	0.70	9.31	0.28	
		(206)	6.75	0.96	1.91	0.54	
5	KDP(Cr)	(800)	7.81	0.96	1.54	0.25	12.0
		(008)	7.82	0.69	9.30	0.27	
		(206)	6.74	0.95	1.90	0.53	
6	KDP(H_2O_2)	(800)	7.80	0.96	1.52	0.26	5.2
		(008)	7.75	0.69	9.19	0.27	
		(206)	6.66	0.95	1.88	0.53	

same method at constant temperature and preset supersaturation from one and the same batch of raw material, where the total content of the controlled impurities (37 elements) was about $2.6 \cdot 10^{-3}$ wt. %. From this raw material, KDP crystals were also grown with purposefully added impurities (Ca, Si, Pb, Cr and hydrogen peroxide), the content of those in the grown crystals was $2 \cdot 10^{-3}$–$5 \cdot 10^{-3}$ wt. %, respectively. Hydrogen peroxide was added to the solution in the amount about 0.1 wt. %. The bulk laser damage threshold for laser radiation at $\lambda = 1.06$ μm and $\tau = 10$ ns was measured for the grown crystals. Samples for investigations, 20×20×20 mm^3 in size, oriented along the {100}, {010}, {001} planes at an accuracy of $<0.05°$, were cut with a thread saw wetted in water and treated by a standard method. The structure quality of grown KDP crystals was studied using a three-crystal X-ray diffractometer (TXD). A new TXD was constructed on the basis of a standard X-ray apparatus DRON-2 [3]. CuK_α radiation monochromated by dislocation-free crystalline germanium monochromators with {333} reflection were used. Mainly utilized was the (n, n, $-m$) arrangement scheme of monochromators and the sample which allowed to work in plane-polarized radiation with minimal spectral and angular dispersion and angular resolution less than 1 arcsec. This also provided a possibility to minimize the reproduction error of the shape and halfwidth of diffraction reflection curves (DRC), β, and the increase the integral reflection power, I^R, up to 2 %. To increase the information volume of the methods used, the linear scanning of the sample was used with respect to the incident X-ray beam of 0.05 to 0.1 mm in diameter, at the scanning step of 0.05 to 2 mm (L-scanning). This allowed to obtain dependences of structure sensitive characteristics β, I^R, $\Delta d/d$ over the sample cross-section: (β(L), $I^R(L)$, $\Delta d/d(L)$). For a precise determination of crystal lattice periods, the character of $\Delta d/d(L)$ a variation of the method developed before [3] was used. Its idea consists in a simultaneous illumination of two crystals with the X-ray beam. One of them is the crystal under investigation and the second one is the reference made of the same material and having the same crystallographic orientation as the first sample. The $\Delta d/d$ determination relative error was about $2 \cdot 10^{-7}$.

Processing of the experimental data for the studied samples has shown that, in spite of the fact that the crystals were grown by one and same method, preset temperature,

degree of supersaturation of the solution, mixing manner, value of pH = 4.5, same batch of raw material, Ca, Si, Pb, Cr and hydrogen peroxide additives effect significantly the structural quality, crystal lattice parameters, and bulk laser damage threshold of the grown crystals.

Table 1 shows the averaged values of the rocking curves halfwidth β for different reflections {hkl}, integral reflection I^R, for 20 measurements carried out in different crystal parts, the standard deviation σ_β, $\sigma_I{}^R$ of those values, as well as values of bulk laser damage threshold P (J/cm^2). An essential inhomogeneity of structure-sensitive parameters over the crystal cross-section is seen: the σ_β and a $\sigma_I{}^R$ values are significantly higher for crystals grown with added impurities and characterized by low values of bulk laser damage threshold.

The analysis of diffraction reflection curves obtained using TXD for the samples grown from a nominally "pure" raw material and having maximum value of bulk laser damage threshold has shown that those are as a rule smooth while for crystals grown with impurities, typical is breaking up of the curves and presence of several maxima angularly spaced by 1 to 3 arcsec. The origin of low-angle turns is explained by the layer-by-layer growth mechanism of the crystals. The low-angle quasi-boundaries separating those layers are formed due to accumulation of impurities on the growing crystal facets. Then a partial violation of coherence occurs between the layers of normal growth. This may result in an additional increase of the layers turn angle with respect to the orientation of the grown crystal [4]. The impurity added crystals have a higher concentration of quasi-boundaries. Addition of impurities to the solution results in their inhomogeneous trapping and distribution over the crystal volume. This results not only in formation of the striated impurity structure but also in a variation of crystal lattice parameters and elastic stresses in the volume of the grown crystals. The authors performed relative precision measurements of the crystal lattice parameter variations Δa, Δb, Δc, unit cell volume of the ΔV, orthorhombicity degree $\Delta = b-a$ and $\Delta d/d$ for crystallographic directions [100], [010] using the method described in [5]. These parameters are presented in Table 2. A sample grown from nominally "pure" raw material and having the maximum value of bulk laser damage threshold was taken as a reference for the measurements.

As it is seen from Table 2, variations of the measured parameters and presence of orthorhombicity are observed for all crystals under investigation. Values in Table 2 are averaged over 20 measurements and were taken in different points of the crystal. Appearance of orthorhombicity that does not vary the symmetry of KDP crystal is presumably stipulated by the character of entry and distribution of impurities, and anisotropy distorting the KDP crystal lattice.

Using a high resolution X-ray diffraction method, it has been shown that addition of Ca, Si, Pb, Cr, hydrogen peroxide to the nominally "pure" raw material results in variation of crystal lattice parameters and deterioration of crystal structure quality. This, in turn, decreases the bulk laser damage threshold and increases the spread in these values over the crystal volume. It has been found that the main growth defect of KDP structure at zonarity and sectoriality absent and dislocation density $\leq 10^2$ cm^{-2} is the impurity striation and presence of low-angle quasi-boundaries. These defects are caused by fluctuations in the growth processes resulting in aninhomogeneous entry

Table 2. Variations of crystal lattice parameters

N	Sample	Δa, 10^{-4} A	Δb, 10^{-4} A	Δc, 10^{-4} A	ΔV, 10^{-2} A^3	$\Delta = b-a$, 10^{-4} A	$\Delta d/d \cdot 10^5$		
							[100]	[010]	[001]
1	KDP(2)	–	–	–	–	0.73	–	–	–
2	KDP(Ca)	8.00	10.36	−1.77	8.05	2.36	10.74	13.80	3.98
3	KDP(Si)	−0.70	0.90	−9.22	−5.00	1.60	0.93	6.07	13.23
4	KDP(Pb)	−1.13	0.70	−7.03	−4.13	1.83	1.52	2.30	10.08
5	KDP(Cr)	−0.90	0.80	−8.12	−4.57	1.70	1.22	1.07	11.76
6	KDP(H_2O_2)	−0.72	1.50	6.32	3.90	2.22	0.97	2.04	9.06

and distribution of impurities in the crystal volume and in the formation of low-angle turns at a layer-by layer growth. A correlation has been revealed between the concentration of low-angle quasi-boundaries, dispersion of structure-sensitive parameters and the bulk laser damage resistance in the grown KDP crystals.

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Зміни параметрів кристалічної гратки монокристалів KDP, які містять домішки

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Кристали KDP, вирощені з водних розчинів циркуляційним методом з номінально "чистої" сировини та сировини з домішками Ca, Si, Pb, Cr та пероксиду водню, досліджено методом рентгенівської дифрактометрії високого розрішення. Показано, що додаткове введення домішок приводить до погіршення структурної досконалості кристалів. Основними дефектами росту кристалів при густині дислокацій ~10^2 $см^{-2}$ та при відсутності зонарності й секторіальності є домішкова смугастість і наявність малокутових квазіграниць. Спостерігається кореляція між концентрацією малокутових квазіграниць, дисперсією структурно-чутливих параметрів і об'ємною лазерною міцністю кристалів.