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Effect of growth conditions on structure quality of KDP crystals

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Abstract. The effect of different variable crystallization parameters (supersaturation, solution acidity, degree of the solution purity, hydrodynamic growth regime) on structural quality and optical homogeneity of KDP crystals grown at the angle of synchronism $\theta = 59°$ was studied by using X-ray analysis and UV spectroscopy. It is shown that each of the chosen parameters acting in a certain way changes (with the rest being constant) the real structure and optical characteristics of crystals.

Keywords: KDP, single crystals, real structure, crystallization parameters, optical absorption, laser damage threshold.

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1. Introduction

The growth process and the quality of KDP crystals significantly depend on supersaturation, solution acidity and its impurity composition since it is crystallization conditions that finally define the presence of different defects and their distribution in the volume of crystals[1–4]. The works devoted to the study of the crystallization condition effect on the real structure and optical homogeneity of KDP crystals grown at the angle of synchronism $\theta =$ 59° are absent in literature. This paper is focused just to the mentioned problem.

2. Experimental

KDP crystals were grown in the direction of a prespecified angle of synchronism $\theta = 59°$ by the temperature lowering method.

The temperature was maintained with an accuracy of 0.05 C°. Raw material with the content of impurities on the level of 5×10^{-5} was used in all the experiments. While one of the parameters was varied the other were remained constant.

Crystalline samples, $20\times20\times20$ mm^3 in size and with the polished planes normal to the crystallographic axes of crystals x, y, z, were used for the study.

Structural quality of crystals was studied by three-crystal X-ray diffraction method of high resolution.

3. Results

3.1. The effect of the solution purification degree from mechanical and colloidal impurities of structural quality on KDP crystals

Shown in Table 1 are the results of structural quality study of orientated crystals grown from the solutions subjected to different degrees of purification.

As one can see from Table 1, the oriented KDP crystals, grown from the solutions purified using 0.05 μm filters, possess a higher structural quality as compared to other crystals. The high optical quality is also confirmed by the absorption spectra of these crystals shown in Fig. 1.

3.2. The effect of the solution pH on structure quality of KDP crystals

The results of the study of structural quality of crystals grown from solutions with different value of pH are shown in Table 2.

As it is seen from Table 2, Figs 2 and 3, crystals grown from solutions with pH = 5 have the highest structural quality; those grown at pH = 2÷4 have a pronounced impurity – a striated structure observed as the splitting of the diffraction reflection curve (DRC) into 20–40 separate peaks with the turn angles of 0.5÷3 arcsec (Fig. 2). The width of the crystal parts that gives low angle turns is

Table 1. Structural quality of oriented crystals grown from the solutions subjected to different degrees of purification

Sample	$\overline{\beta}$				$I^R \cdot 10^6$ rad			
	(800)	(080)	(008)	(206)	(800)	(080)	(008)	(206)
∅ = 0.05 μm, [001]	5.98	6.25	7.22	6.76	4.12	5.02	9.63	1.08
∅ = 0.05 μm, [100]	6.81	8.14	10.85	5.99	4.32	4.96	9.84	1.27
∅ = 0.15 μm, [001]	7.97	8.04	7.66	6.01	5.34	5.43	9.17	1.22
∅ = 0.15 μm, [100]	10.02	10.34	8.42	7.52	5.23	5.30	9.30	1.16
standard*	6.09	6.48	7.84	6.04	4.88	4.98	10.05	1.00

Table 2. Structure quality of crystals grown from solutions with different value of pH

Sample	$\overline{\beta}$				$I^R \cdot 10^6$ rad			
	(800)	(080)	(008)	(206)	(800)	(080)	(008)	(206)
pH=2, [001]	8.95	17.9	8.54	5.66	4.79	4.81	6.95	0.80
pH=2, [100]	20.12	24.02	11.9	11.16	6.49	5.56	8.56	0.91
pH=4, [001]	9.2	9.6	8.22	6.02	6.60	6.62	8.50	0.92
pH=4, [100]	10.3	26.5	8.36	6.08	6.75	6.8	9.14	1.04
pH=5, [001]	7.15	7.22	7.25	6.22	5.58	6.62	9.61	1.17
pH=5, [100]	7.46	9.10	8.44	6.42	5.62	6.70	9.64	1.20
standard	6.09	6.48	7.84	6.04	4.88	4.98	10.05	1.00

0.1÷20 μm, with the assumption that the intensity in the maximum of DRC is proportional to the cross-section of crystal parts for each peak. The formed impurity-striated structure at the growth in the direction [100], [010] (Fig. 2a) produces a significant effect on structure quality of crystals grown simultaneously in the direction [001] (Fig. 2b), i. e. one can observe the inheritance of the faulty structure by the crystal growing simultaneously in the direction [001].

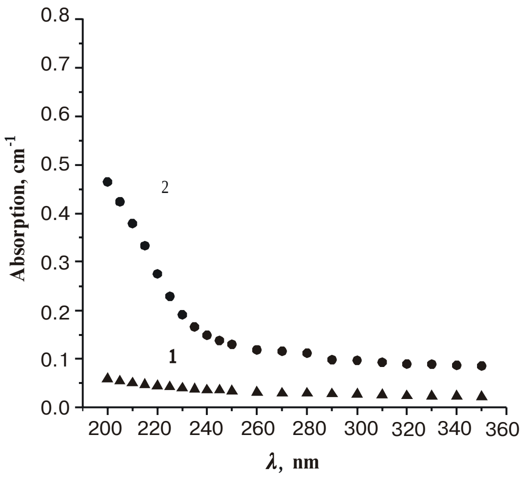

Fig. 1. Absorption spectra of KDP crystals in dependence on the filter pores sizes: 1 - ∅ = 0.05 μm; 2 - ∅ = 0.15 μm.

In crystals without a zone-sectorial structure and with density of dislocation not exceeding 10^2 cm^{-2} one could practically always observe quasi-boundaries on DRC, those giving low angle turns at a resolution of TXD 0.5 arcsec.

Thus, the main growth defects of KDP structure (crystals grown in 3 directions) are the impurity striation and low angle quasi-boundaries. A correlation between concentration of low angle boundaries, dispersion of structure sensitive parameters and optical characteristics was found.

High quality of crystals grown from the solutions with pH = 5 is confirmed by absorption spectra of these crystals (Fig. 3).

3.3. The effect of the solution supersaturation on structural quality of crystals

The total results of the study of structural quality of KDP crystals grown at different supersaturations σ = 2 % and 4 % are presented in Table 3.

As it is seen from the Table 3, the structural quality of crystals grown at supersaturation σ = 2 % is a bit better than of those grown at σ = 4 %. The decrease of the halfwidth of the rocking curve β and values of the integral power of reflection I^R is typical for crystals grown at small supersaturations. High quality of crystals is confirmed by the absorption spectra (Fig. 4).

Table 3. Structure quality of KDP crystals grown at a different supersaturations

Sample	$\bar{\beta}$				$I^R \cdot 10^6$ rad			
	(800)	(080)	(008)	(206)	(800)	(080)	(008)	(206)
$\sigma = 2\%$	6.92	7.04	10.6	7.7	4.58	6.03	10.4	1.11
$\sigma = 4\%$	7.60	7.70	11.8	6.45	5.3	5.96	11.15	1.14
standard	6.09	6.48	7.84	6.04	4.88	4.98	10.05	1.00

Table 4. Structure quality of KDP crystals grown at a different seed rotation rates

Sample	$\bar{\beta}$				$I^R \cdot 10^6$ rad			
	(800)	(080)	(008)	(206)	(800)	(080)	(008)	(206)
30 rev./min	26.4	28.60	8.33	7.39	5.49	5.58	10.09	1.11
10 rev./min	19.84	20.93	7.69	5.91	6.04	6.22	9.25	1.18
standard	6.09	6.48	7.84	6.04	4.88	4.98	10.05	1.00

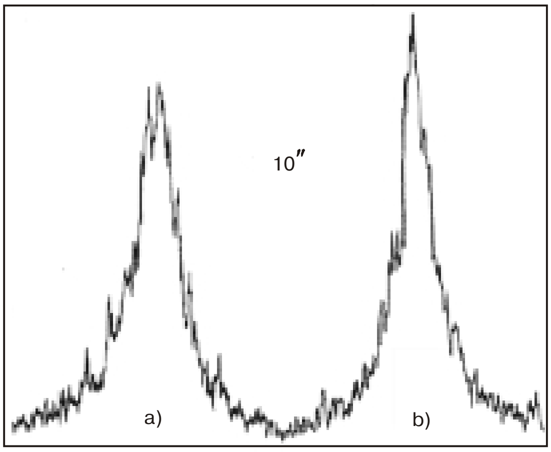

Fig.2. The form of diffraction reflection curves registered on TXD; KDP, pH = 2, CuK_α - radiation; a - reflection {800}; b - reflection {206}.

3.4. The effect of the mixing conditions on structural quality of crystals

The results of the study of structural quality of KDP crystals grown at a seed rotation rate 10 rev./min and 30 rev./min are shown in Table 4.

As the Table 4 shows, crystals grown at a seed rotation rate 10 rev./min have better quality. As for the absorption spectra (Fig. 5) the lowest absorption is inherent to crystals grown at a seed rotation rate 30 rev./min.

The analysis of the experimental data showed that in crystals grown under mixing conditions 10 rev./min the concentration of liquid inclusions was by an order higher than in those grown under 30 rev./min. Perhaps, the presence of a big amount of liquid inclusions lead to a worsening of transmission but is not followed by any decreasing of structural quality of crystals.

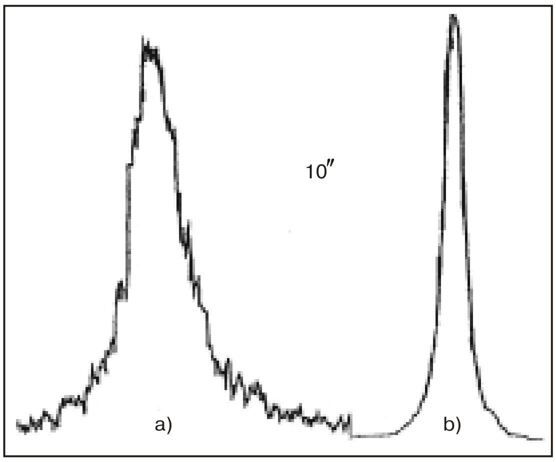

Fig. 3. The configuration of diffraction reflection curves obtained for reflection (800): a - pH = 2.0; b - pH = 5.0.

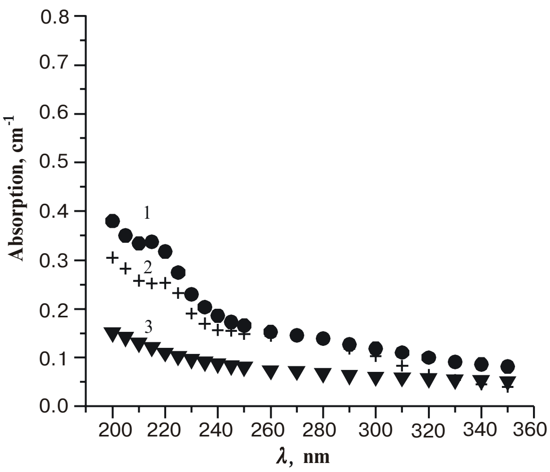

Fig. 4. Absorption spectra of KDP crystals grown at different values of pH: 1- pH = 2.0; 2 - pH = 4.0; 3 - pH = 5.0.

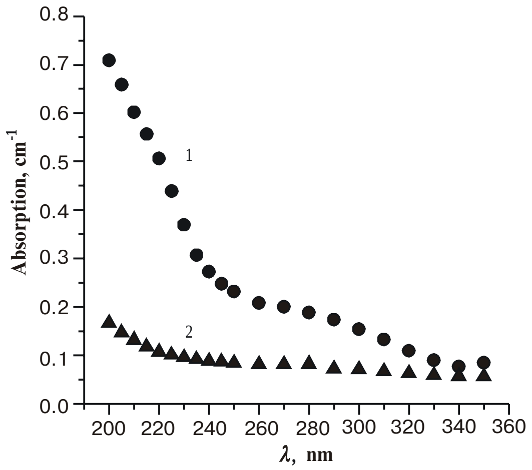

Fig. 5. Absorption spectra of KDP crystals in dependence on the supersaturation of the solution: 1 - $\sigma = 4\%$; 2 - $\sigma = 2\%$.

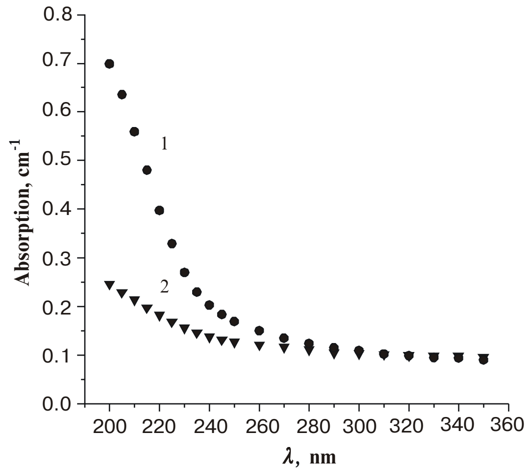

Fig. 6. Absorption spectra of KDP crystals in dependence on the rotation rate of the crystal: 1 - 10 rev/min; 2 - 30 rev/min.

Conclusions

On the basis of the analysis of growth conditions and crystals quality the optimal growth regimes of KDP crystals were determined, crystals being 200 mm in cross-section. It was found that the best crystallization parameters for high quality crystals growing are as follows:

- raw material with the content of polyvalent metals on the level of 1×10^{-5} mass %;
- supersaturation 2%;
- crystallization temperature 60 °C;
- pH = 5;
- rate of solution mixing not less than 30 rev./min.;
- purification of solutions by using filters with a diameter of pores about 0.05 μm;
- the main growth defects of KDP structure (crystals being grown in three crystallographic directions) are the impurity striation and low angle quasi – boundaries.

A correlation between the concentration of low angle boundaries, dispersion of structure sensitive parameters and optical characteristics were established.

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