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Research of Structural Quality of Big-Size KDP Crystals

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Abstract. The faulted structure formation at a rapid growing of big-size KDP crystals has been analyzed. A transitional zone with high degree of lattice faultness has been revealed between the seed and the pure zone of the grown crystal by X-ray diffraction methods with high resolution. It has been determined that, regardless of the seed form, the transitional layer in grown crystals reaches the value of~12 mm. The nonmonotone variation of the crystal lattice parameter ($\Delta d/d$) within $\pm 2.5 \cdot 10^{-5}$ and the halfwidth of a diffraction reflection curve ($\beta = 5.5 \div 8$ arcs for direction [103] and $\beta = 7 \div 9$ arcs for direction [100]) and the increase of the integral power of reflection of the X-ray beam I^R by 1.5 times are observed in the transitional layer.

Keywords: KDP single crystals, structural quality, X-ray diffraction, crystal lattice parameter.

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1. Introduction

Formation of inherent lattice defects in the process of growth of potassium dihydrogen phosphate (KDP) crystals leads to a considerable change of the characteristics of wide-aperture nonlinear elements at the influence of the high-power laser irradiation with a radiation density energy of ~ 50 J/sm^2 on them.

Development of sensitive X-ray methods of crystal research gives a possibility to determine the correlation between the crystal characteristics and parameters characterizing their structural quality [1, 2].

Seed crystals of various forms and crystallographic orientations are used for the KDP crystal growth. As a result of the seed growth, the defects located on its surface are inherited by the growing crystal. This influences considerably the structural quality of the grown crystal, its optical homogeneity, and the bulk laser damage threshold. This effect is observed especially when KDP crystals grow in directions [100] and [010] of a prism [3, 4]. We would like to note that most of the work done [5, 6] is devoted to the research of the dislocation structure of grown crystals. No information concerning the research of the transitional layer and its influence on the subsequent growth of the crystal is available.

Here, we present the results of X-ray diffraction studies of a structural quality of the transitional zone «seed - grown crystal» formed at the initial growth stage.

2. Experimental methods

Big-size KDP crystals were grown from the water solutions by the method of solvent recirculation on various kinds of seeds: pyramidal seeds, point seeds with facet orientations [001], [100], and [010], as well as on the Z-cut plate. For the investigations carried out, the experimental samples of 50×50×50 mm^3 in size which had been cut out from various parts of the grown crystals with a section of 300×300×300 mm^3 were used. The samples were oriented in the crystallographic directions [001], [100], and [010] with an accuracy of 0.05º and then were subjected to the standard chemical and mechanical treatment providing the strained layer thickness which did not exceed 2 µm.

Structural investigations were conducted by the method of sensitive three-crystal X-ray diffractometry (TXD) in Cuk$_{\alpha 1}$-radiation [1]. The depth of X-ray beam penetration into the crystal amounted to dozens of microns. Higher diffractometer measurement precision was achieved by the formation of the initial X-ray beam with small angular and spectral divergence which allowed us to obtain diffraction reflection curves (DRCs) having the halfwidth ß = 7÷10 arcs. This method gives a possibility to minimize mistakes of the reproduction of the form and the halfwidth of DRC ß and the value of the integral power of reflection of the X-ray beam I^R, as well as to increase the accuracy of the lattice parameter determination to $2 \cdot 10^{-7}$, while values of ß, I^R, and $\Delta d/d$ are used as the measure of the structural perfection of the grown crystals. Linear scanning of the

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sample relative to the initial X-ray beam (L-scanning) having a step of 0.05÷2 mm allows us to obtain the dependence of these parameters on the cross section of a crystal.

When conducting the X-ray diffraction investigations of the crystal samples, both symmetric and asymmetric Bragg reflections were used. Investigations of crystals grown on the various kinds of seeds were conducted in four crystallographic directions ([001], [100], [010], and [103]) in three typical areas: the seed, the transitional zone, and the grown crystal. The rocking curves from reflections {600}, {060}, {008}, and {206} were registered.

3. Results and discussion

Fig. 1 a-d shows the character of variations of the rocking curve halfwidth at the L-scanning of a KDP crystal grown on a pyramidal seed.

As one can see from Fig. 1, a significant nonmonotone dependence ß(L) is observed, especially, in the area between the grown crystal and the seed (transitional zone), the width of which is about 12 mm. In this area, all the DRCs have from 2 to 30 separate maxima which are caused by the presence of low-angle quasi-boundaries with turn angles of 0.5±4 arcs. This effect can be explained by fluctuations of the growth rates by a layer-by-layer crystal growth mechanism. As a result of growth rate fluctuations, the nonuniform trapping and the spreading of polyvalent metal impurities such as Cr^{3+}, Fe^{3+}, Al^{3+}, Ti^{4+}, etc. in the transitional zone occur in the growing layers.

The mean concentration of trapped impurities in this area of the crystal does not differ essentially from the concentration of impurities in other zones such as the seed and the grown crystal. However, an insignificant local excess of the impurity content in the transitional zone can lead to the crystal coloration. The authors visually observed a colored band in the growing crystal of about 3 mm. The optical absorption value of the colored zone is 3-4 times higher than that in the seed or the grown crystal. It should be noted that the width of this zone observed at the X-ray diffraction analysis is 4 times larger than that at a visual registration or by optical absorption spectra.

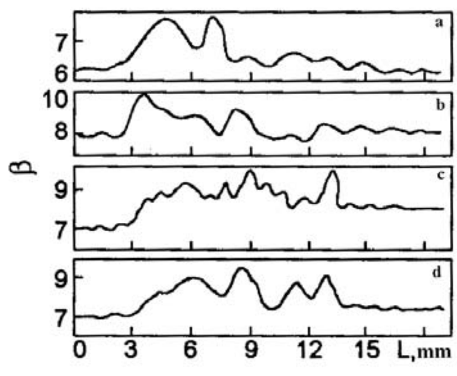

Fig. l. Variation of β(L) for KDP crystals grown on pyramidal seeds: *a* – reflection {600}, direction [100], *b* – reflection {060}, direction [010], *c* – reflection {008}, direction [001], *d* – reflection {206}, direction [103].

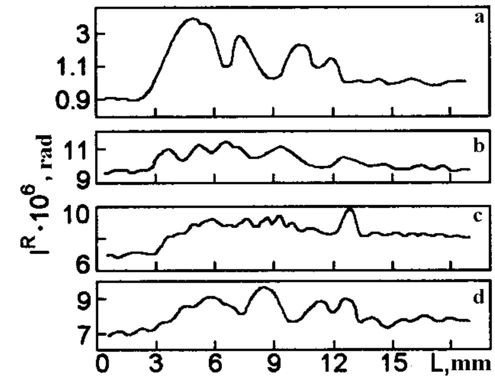

Fig. 2. Variation of $I^R(L)$ for KDP crystals grown on pyramidal seeds: *a* – reflection {600} direction [100], *b* – reflection {060}, direction [010], *c* – reflection {008}, direction [001], *d* – reflection {206}, direction [103].

The X-ray diffraction methods of investigations fix the presence of the transitional zone even if it is not seen visually on the spectra of optical absorption. The authors have found the increase of the integral reflection power of the X-ray beam I^R for this part of the crystal (Fig. 2, a-d).

Thus, in the zone neighboring to the crystal and the seed (transitional zone), we have established the presence of an impurity-striated structure which leads to the splitting of DRCs and the increase of the content of structural defects yielding an increase of the integral reflection power I^R.

The authors also investigated the behavior of Δd/d in three areas: the seed, the transitional zone, and the grown crystal. The results of these measurements for the crystallographic direction [100] are shown in Fig. 3. As one can see from Fig. 3, the oscillations of Δd/d for the transitional zone are$\pm 2.5\cdot10^{-5}$. At the same time, the variation of Δd/d in the seed does not exceed $\pm5\cdot10^{-6}$, while it is $\pm5\cdot10^{-6}$ in the grown crystal in the studied area. In the grown crystal, the authors found the increase of $\Delta d/d$ by the value of $\pm1\cdot10^{-5}$ with respect to the seed.

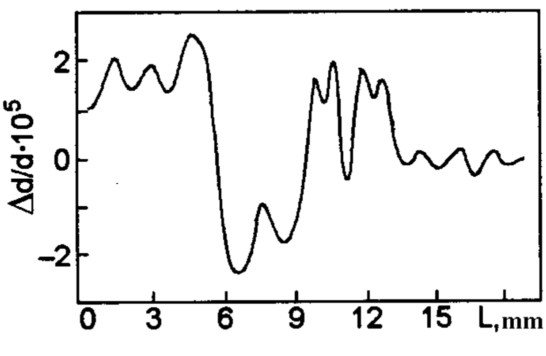

Fig. 3. Variation of Δd/d(L) for KDP crystals grown on pyramidal seeds, reflection {600}, crystallographic direction [100].

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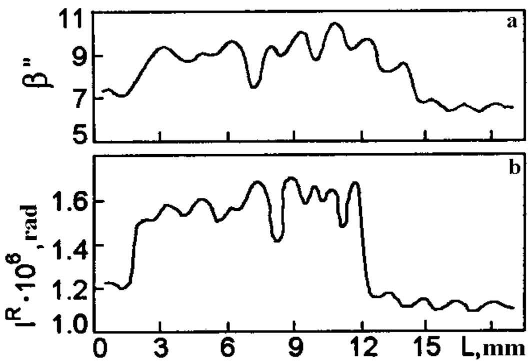

Fig. 4. Variation of β(L) and I^R(L) for crystals grown on plane seeds: *a* - β(L) reflection {206}, direction [103]; *b* - I^R(L) reflection {206}, direction [103].

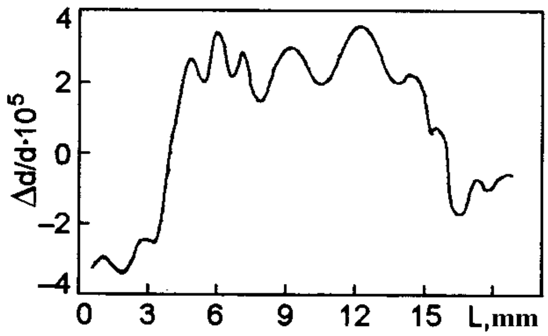

Fig. 5. Variation of Δd/d(L) for KDP crystals grown on plane seeds, reflection {600}, direction [100].

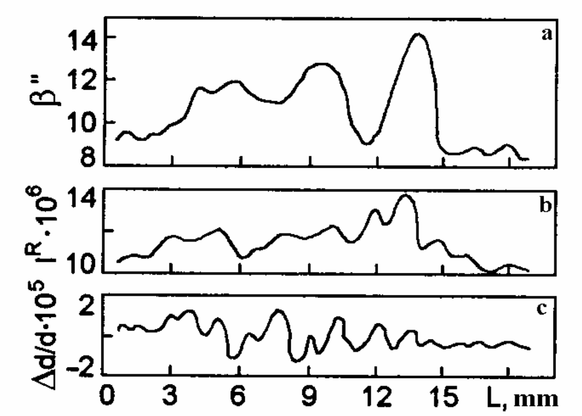

Fig. 6. Variation of β(L) – (*a*), I^R(L) – (*b*), Δd/d(L) – (*c*) for KDP crystals grown on point seeds in the crystallographic direction [100].

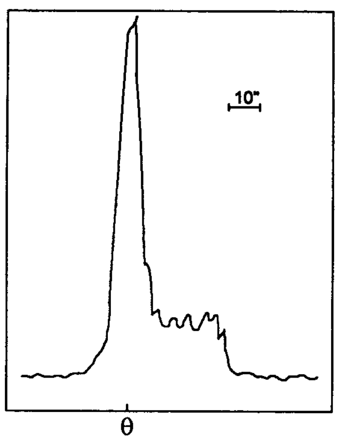

Fig. 7. The form of the rocking curve of the parts of a KDP crystal grown on a point seed in the crystallographic directions [100] and [010]; $Cuk_{\alpha 1}$, -radiation, reflection {008}.

The analogous picture is also observed for KDP crystals grown on plane seeds. In Fig. 4 a, b, we show the dependences ß(L) and I^R(L) for reflection {206} in the crystallographic direction [103]. The transitional zone of about 10 mm in width is characterized by the increased content of structural defects resulting in the splitting and smearing (broadening) of DRCs and an increase of the integral reflection power I^R. The authors associate the higher values of ß and I^R, as compared with analogous values obtained for the crystals grown on the pyramidal seeds, with the quality of a crystal used as a plane seed. The variation of Δd/d for the transitional zone in the case of crystals grown on the plane seed was $\pm 3.5 \cdot 10^{-5}$. The variation of the Δd/d value on the seed did not exceed $\pm 5 \cdot 10^{-6}$, and it was $\pm 5 \cdot 10^{-6}$ on the grown crystal (Fig. 5). The parameter Δd/d of the seed exceeded that of the grown crystal by the value of $2.5 \cdot 10^{-5}$.

KDP crystals grown on the point seed have also the area with an elevated content of structural defects, which results in a nonmonotone variation of ß (L), I^R (L), and Δ*d*/d(*L*) in this part (see Fig. 6 a, b, c). The presence of an angular turn of about 32 arcs between two prismatic growth sectors was also revealed in these crystals. Figure 7 shows a rocking curve (reflection {008}) for the case of a simultaneous incidence of the beam onto the parts of the crystal, whose growth proceeded in the crystallographic directions [100] and [010]. This figure clearly demonstrates the anisotropy of the impurity-striated structure in different crystallographic directions.

The X-ray diffraction investigations of the structural quality in the "crystal - restrictive plane" zone conducted by the authors did not reveal a strained layer similar to the transitional "crystal – seed" zone. In the "crystal - restrictive plane" zone, the layers with increased content of the structure defects with a size amounted to ~10 μm were revealed. Such strained layer does not influence the characteristics of both frequency multipliers for laser emission and Pockels cells produced of fast-frown KDP crystals in the direction of a given synchronism angle. The strained layer can be removed in the process of the optical and mechanical treatment of the crystal.

The X-ray diffraction investigations of a fine faulty structure in the bulk of KDP crystals showed that the structural defects formed at the stages of crystal growth in directions [100] and [010] are partially inherited by the crystal growing in direction [001]. The splitting of DRCs

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and an increase of ß and I^R which were observed during the investigations are caused by the impurity-striated structure and the formation of low-angle boundaries by a layer-by-layer mechanism of crystal growth. These structural defects are formed under fluctuations of the growth parameters and significantly deteriorate the bulk laser damage threshold of KDP crystals [7].

4. Conclusions

While growing crystals from aqueous solutions on the seeds of various forms (pyramidal, plane, and point-like ones), a transitional zone with increased concentration of structural defects is formed between the seed and the grown crystal. It is characterized by a nonmonotone variation of the rocking curve halfwidth, integral reflection power of the X-ray beam, and crystal lattice parameter in the limits of $\pm 2.5 \cdot 10^{-5}$. This area reaches 12 mm. The impurity-striated structure with quasiboundaries and angular turns of 0.5÷4 arcs is clearly expressed in it.

At a break of the growth process, the further growth of the crystal proceeds through the zone with increased content of structural defects. The presence of the angular turn of about 30 arcs was found between the parts of the crystal, whose growth proceeded in directions [100] and [010]. In the process of crystal growth in the crystallographic directions [100] and [010], the formed faulty zone can be inherited by the growing crystal in direction [001].

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