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Section 1: Single crystal materials

OPTICAL CHARACTERIZATION AND LASER DAMAGE THRESHOLD OF RAPIDLY GROWN KDP CRYSTALS

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Transparency of a KDP crystal grown at a rate of V=15 mm/day has been studied in a wide wavelength range. A noticeably nonuniform distribution of the absorption coefficient k over crystal volume has been found in the UV part of the spectrum. In the visible and IR parts the difference in the k values for different points of the crystal is much less. Using a pulse YAG:Nd^{3+} laser (λ=1064 nm, τ=10 ns)the authors measured the value of laser damage threshold (W) for the samples cut of the growth sectors {100} an {101}. The obtained results showed an insignificant difference in this value (1.5-2 Gwt/cm^2) for different growth sectors. Measurements of electrophysical characteristics and, specifically, electrical resistivity ρ demonstrated its dependence on chemical composition of the samples and their distance from the point seed. A correlation between the measured values has been found. A comparison of the corresponding values k, W and ρ for rapidly and traditionally grown crystals has been made.

Keywords: KDP single crystals, Structural quality, Impurities, Optical absorption, Laser damage threshold

1. Introduction

Crystals of the KDP series still remain practically the only materials that are successfully used as optical gates and frequency multipliers in laser systems for the controlled nuclear fusion. This circumstance has naturally stimulated development of new rapid crystal growth methods which would make the growth cycle essentially shorter while preserving optical quality typical for "traditional" crystals [1, 2, 3].

Accelerating crystal growth makes sense only provided optical and structural quality of the obtained crystals remains on a high enough level. Therefore quality of crystals is one of the decisive points in the rapid growth method.

When crystals are grown from the point seed they contain facets both of a pyramid and those of a prism, this being conditioned by its morphology. Due to this fact foreign ions enter the growing crystal from the solution quite differently. This is explained by a different adsorption ability of crystal facets. All together define the final quality level of the grown crystals [4].

Studied in this paper were regularities of distribution of the absorption coefficient value k in the UV and IR parts of the spectrum in different growth sectors of the facets {100} and {101} of the rapidly grown KDP crystal. The changes in the value of laser damage threshold have been analyzed as a function of distance L from the seed to the peripheral part of the crystal. A correlation between the resistivity value, absorption spectra in the UV part and chemical composition of the studied crystals has been found.

2. Experiment

Used for the study was KH_2PO_4 salt with the content of Fe, Cr - $5\cdot10^{-5}$; Al - $5\cdot10^{-4}$ мас%. The impurity content in the samples was determined by atomic-emission spectral and chemical analyses.

For the investigation, KDP crystals were grown from aqueous supersaturated solution on a point seed by a temperature cooling method from solutions filtered through a 0.15 μm teflon membrane. The pH of the solution saturated at 60°C were 4.2. The crystals were grown in the thermostated crystallizer of 5-l capacity with an automatic temperature controlling to an accuracy of ±0.05° C. The crystal rotates in the mode of "forward-stop-backward" with a speed of 30 rpm. The size of final grown crystal was 70x70x100 mm^3 of which an average growth rate was 15 mm/day.

For all experiments samples was cut with dimensions 15x15x15 mm^3 from the zone close to the seed and other samples from the zone far from the. All samples included some part of the pyramidal and some part of the prismatic growth sector of the crystal. After this the samples were polished to optical quality. The regions of the original crystal that were used as the samples are illustrated in Fig. 1.

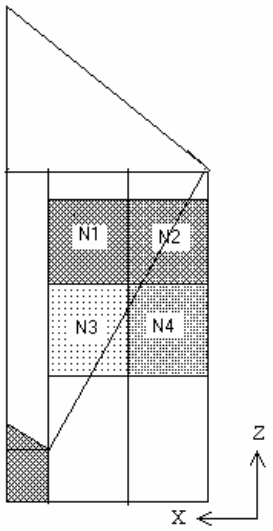

Fig. 1. Schematic drawing of an Y cut of the crystal, showing the regions which were sawed for the samples.

3. Characterization

3.1. Optical absorption

The transmission was measured by UV-V-NIR automatic scanning spectrophotometer SF -56 (LOMO) at room temperature in the wave range of 0.2-1.1 μm. The absorption coefficient was calculated at a known thickness of the sample without an account of Fresnel reflection.

When crystals are grown from solutions defects like mother liquor and macroparticles' inclusions [5, 6] are most commonly formed on their surface. Another factor having a negative effect on optical quality of crystals is the presence of several facets that grow simultaneously [7]. In KDP-group crystals there is a direct correlation between concentration of the inorganic impurities in the lattice and optical absorption value in the near UV part of the spectrum [6, 8, 9]. Therefore, while studying the latter one can receive sufficiently full information about chemical purity of a particular sample. Even in the first experiments on rapid growth noted was the difference in the absorption spectra of crystals grown along the prism and pyramid facets. It was assumed to be caused by different adsorption ability of these facets with respect to impurity ions present in the solution.

As a rule, the absorption spectra of rapidly grown KDP crystals are characterized by the absorption band at 270 nm in the UV part. It has been shown in [6, 7] that this band appears due to the entrance of trivalent metal impurities to the KDP crystal lattice.

Table 1. Concentrations of some cations for the different KDP samples , the amount of Pb, Sn, Ni, Co and Mo was $<2\cdot10^{-4}$.

Sample	Fe	Mg	Si	Al	Cu	Cr
1.	$5\cdot10^{-5}$	$2.5\cdot10^{-4}$	$<1\cdot10^{-3}$	$5\cdot10^{-4}$	$2.5\cdot10^{-5}$	$5\cdot10^{-5}$
2.	$2.2\cdot10^{-4}$	$3.5\cdot10^{-4}$	$<1\cdot10^{-3}$	$1\cdot10^{-3}$	$2.5\cdot10^{-5}$	$8\cdot10^{-5}$
3.	$5\cdot10^{-4}$	$3\cdot10^{-4}$	$<1\cdot10^{-3}$	$2\cdot10^{-3}$	$4.5\cdot10^{-5}$	$2\cdot10^{-4}$
4.	$2.5\cdot10^{-4}$	$3.5\cdot10^{-4}$	$<1\cdot10^{-3}$	$2\cdot10^{-3}$	$3\cdot10^{-5}$	$1\cdot10^{-4}$

Fig. 2 shows the UV absorption value at 270 nm as a function of Y (mm) at scanning the samples from the center of the crystal to its peripheral part . For all samples the absorption coefficient in the growth sector {100} does not vary at a distance from the seed part of the crystal [10] and not correlates with the results of investigations [11] in which one can observe a significant change in light transmission with the elongation of the distance from the boundary between prismatic and pyramidal sectors of the crystal (and the seed crystal, respectively).

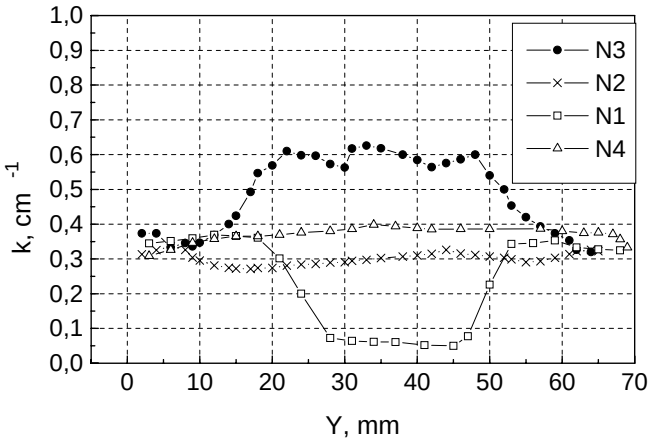

Fig. 2. Absorption coefficient at 270 nm for the different samples as a function of position along Y direction .

In the region of the transitional zone between the sectors prism-pyramid in the sample N3 a dramatic increase of the absorption coefficient (k) from 0.3 cm^{-1} to 0.6 cm^{-1} takes place. At further scanning the value of k smoothly decreases down to 0.55 cm^{-1} and then again rises reaching the maximum value at the point closest to the seed. With this a spectrum typical for the growth sector (100) appears in the region of this sample pyramid, Fig. 3. The appearance of anomalously high absorption in the pyramid sector of the sample N3 is probably connected with the fact that the part of the crystal most closely adjacent to the seed is the most imperfect and is characterized by high density of local stresses [11, 12]. Besides, this part contains the maximum amount of impurities: Fe, Cr, Al (see Table 1).

For the sample N1 the regularity of the absorption coefficient distribution over the section of the sample differs from that of N3. Near the boundary of the sectors one can see a sharp decrease of the absorption coefficient from 0.35 cm^{-1} in the sector {100} to 0.06 cm^{-1} in the sector {001}. Correspondingly, in the region of the pyramid there appears a spectrum (Fig. 3) corresponding to the growth sector {101} in which the band at λ=270 nm is absent and the absorption value is close to that typical for the traditional crystal. The data of the Table 1 give evidence to the fact that this part of the crystal is the least contaminated with the trivalent metal impurities and, consequently is the least faulty from the point of view of optical homogeneity.

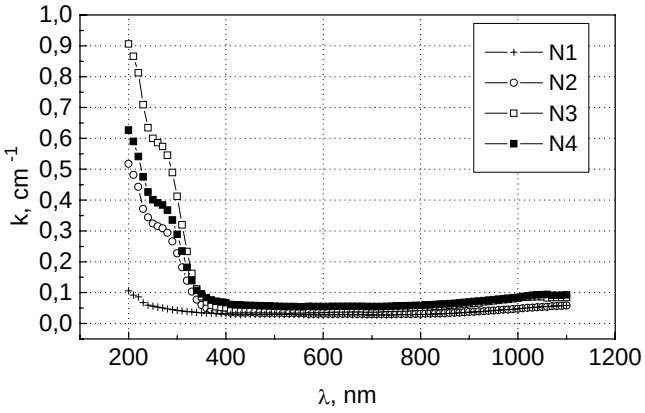

Fig. 3. The absorption spectra of KDP samples from 200 to 1100 nm (for parts of the samples above the seed).

Scanning of the samples N2 and N4 did not reveal any peculiarities in the variation of the absorption coefficient. According to Fig. 2 the absorption in both samples remains on one level and makes 0.3 cm^{-1} in N2 and 0.35 cm^{-1} in N4. From the scheme of crystal cutting it is seen that the sample N2 has the regions both of a pyramid and prism while as the sample N4 – only the sector of a prism. Perhaps, just this makes some difference in their spectra. Therefore the presence of the boundary prism-pyramid is weakly manifested in the spectrum of the sample N2 and the value of k corresponds to the absorption in the sector of the prism (Fig. 3).

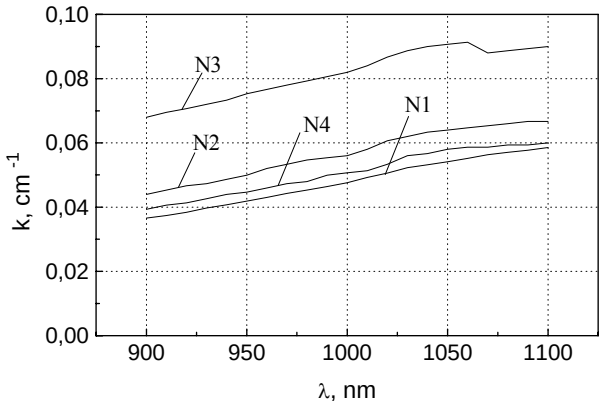

Fig. 4. Variation of IR-absorption of KDP samples.

The absorption spectra in the range of wavelengths 900-1100 nm are presented in Fig. 4. The sample N3 demonstrates an essential increase of absorption as compared to N1 and N2.In all the studied range the absorption value of the sample N3 exceeded 1.5-2 times its value in N1 and N2. Besides, the sample N3 has an absorption band at 1050 nm the intensity of which insignificantly varies at scanning from the center of the crystal to its periphery. Identification of this band is impossible for the present though the authors of the paper [7] made an assumption that the water molecule would incorporate into the lattice due to its growth rate that may increase the absorption by OH vibration at IR region.

3.2 Laser damage threshold

Laser damage threshold was measured with well polished samples obtained in the above experiments using YAG:Nd^{3+} laser. The power of laser radiation was measured with a photodiode, the

signal from which was recorded on PC. The measurements were carried out in the mode of 1-on-1 procedure in which each site of a tested sample was only once irradiated at the conditions of

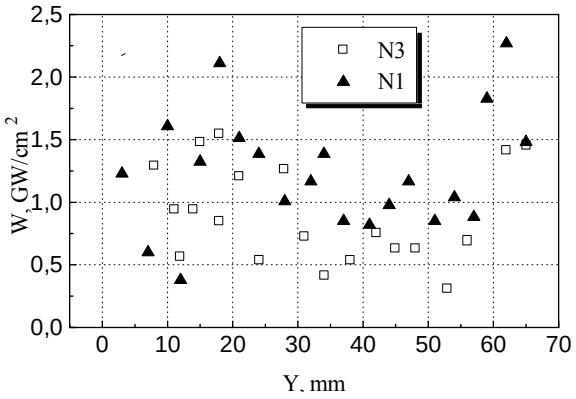

Fig. 5. Laser-induced bulk damage threshold for the samples as a function of position along Y direction.

wavelength 1.064 μm, pulse width 10 ns, focus length 50mm, focus area 50 μm. Indication of damage was made visually by the advent of a spark of a high temperature luminescence of YAG:Nd^{3+}-laser beam in the studied crystals. Laser damage threshold was measured along Z-axis of the crystal.

The results of these measurements are given in Fig. 5. These data show that for all samples there is a noticeable spread in the values of laser damage threshold. The strongest variations of the damage threshold value are observed in the samples N2 and N1 (from 0.7 to 3 Gwt/cm^2. In the samples N3 and N4 the spread in this parameter is twice less (from 0.7 to 1.6 Gwt/cm^2. The reasons of the nonuniformity of the damage threshold distribution are not clear since the presence of such defects as boundaries between sectors does not correlate with the magnitude of W.

3.3 Resistivity of crystals

Electrical conduction of the KDP-group crystals is defined by the transfer of protons inside the frame of hydrogen bonds [13]. Two mechanisms are considered at present: the first is identical to the explanation of conductivity of ice having H-bonds [13], according to the second the conduction is connected with the incorporation of other valence impurities to the crystal lattice and as a result – with the defects that are formed in crystals due to this [14].

Conduction of ice is defined by a simultaneous presence of "+" and "-" ions as well as by the orientational defects – vacant (L-defects) and twice occupied (D-defects) hydrogen bond. The mentioned in literature experimental data allow to assert that conduction of the KDP-group crystals is defined by both: thermally generated L-defects and incorporated into crystal lattice other valence impurities, also generating L-defects [13,10,15].

Elements 15 mm in thickness on which Ag-contacts 5 mm thick were applied by vacuum deposition were used for the determination of resistivity. The measurements were conducted at constant voltage using Ag-electrodes.

The obtained results are shown in Fig. 6. The values of resistivity for all points of the crystal lie in the range of $4 \cdot 10^8$ - $4 \cdot 10^9$ ohm·cm which is somewhat lower than for traditional crystals [10]. It should be noted that the values of ρ differ by an order over the crystal section. This perhaps can be explained by a sectorial structure of the crystal. A nonuniform distribution of impurities in the growth sectors {100} and {101} (Table 1) and distortions of the crystal lattice near the boundary between sectors lead to the differences in the concentration of L-defects which essentially define the resistivity. As it is seen from the figure for all the samples the maximum values of ρ are observed in the central part of the crystal - at a maximum distance from the boundary between growth sectors.

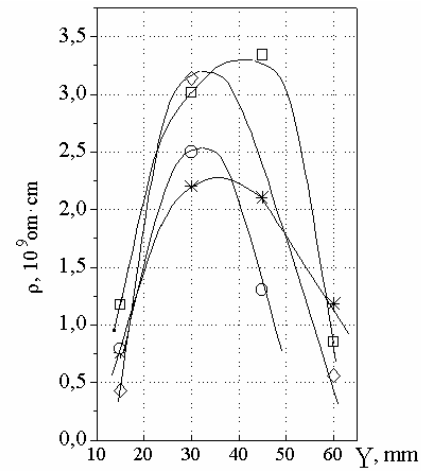

Fig. 6. Electrical resistivity for the samples as a function of position along Y direction:
- N1, - 2, - 3, - N4.

The comparison of the absorption coefficient (k) distributions (Fig. 2) and resistivity ρ over the crystal section (Fig. 6) with the results of the chemical analysis (the samples N1…4) allowed to find out a certain regularity: the purer is the sample the higher resistivity it has and the lower is the absorption coefficient (λ=270 nm). However, to give a final answer to the question about a correlation between these characteristics necessary are further investigations.

4. Conclusions

Using a point seed rapid method a KDP crystal 70x70x100 mm^3 has been grown. The distribution of the absorption coefficient value in a wide range of wavelengths has been analyzed for different parts of the crystal. The found nonuniformity of k distribution is explained by a sectorial structure of the crystal and as, a consequence, different impurity composition of the growth sectors. Resistivity was found to reach its maximum value ($4 \cdot 10^9$ ohm·cm) in those parts of the crystals which are far from the boundaries between sectors. The obtained data give a possibility to find out a certain correlation between optical absorption, electrical resistivity and chemical composition of the samples.

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