Effect of organic dye on the growth and optical properties of KDP

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It is established that *Xylenol Orange (XO)* preferentially dyes the faces {100} and {010} of KDP crystal. The dye content in the crystals is found to be practically independent of its content in the solution. It is revealed that the crystal habit changes in the presence of organic dyes: the ratio of the faces {100} and {010} (**x** and **y**) at maximum concentrations reaches 1.2. Studied is the influence of the mother solution acidity on the character of the crystal coloration. It is established that the color and dyeing intensity depend on the solution's pH. The optical transmission spectrum of KDP with dye (solutions and crystals) is registered. The characteristic absorption peaks are observed in the region from 200 to 600 nm. Revealed is the transmission anisotropy in the directions **x** and **y** for the dyed crystals. Dichroism in KDP + *XO* is shown to depend on the orientation. The emission and excitation spectra of the dyed crystals are measured. The values of bulk laser damage threshold are determined. Discussed is the mechanism of the organic dye incorporation into the crystal matrix.

Выращены кристаллы KDP с добавками органического красителя *Xylenol Orange (XO)*. Показано, что *XO* преимущественно окрашивает грани {100} и {010} кристалла; содержание красителя в кристалле практически не зависит от его концентрации в растворе. Обнаружено изменение габитуса выращенных в присутствии органики кристаллов: отношение размеров граней {100} и {010} (**x** и **y**) при максимальных концентрациях красителя достигает 1,2. Изучено влияние кислотности маточного раствора на характер окрашивания кристалла. Установлено, что в зависимости от pH раствора изменяются как цвет, так и интенсивность окрашивания. Измерены спектры пропускания растворов и кристаллов KDP + *XO* в диапазоне длин волн 200−600 нм. Обнаружена анизотропия пропускания в направлениях **x** и **y** для окрашенных кристаллов. Показано, что дихроизм в KDP + *XO* является ориентационно зависимым. Измерены спектры возбуждения и люминесценции окрашенных кристаллов. Определены величины порога объемного лазерного разрушения. Обсуждается механизм вхождения органического красителя в кристаллическую матрицу.

As is well-known, unique properties of KH_2PO_4 (KDP) crystals make them greatly effective for nonlinear optics and quantum electronics. Nowadays they are widely used in various nonlinear and electro-optical devices such as frequency generators, optical parametric oscillators and electro-optical modulators. These crystals are also very promising for 3D optical data storage. KDP undoubtedly belongs to those crystals which growth mechanism has been thoroughly studied and may serve as a model system for investigating growth mechanisms of crystals. In particular, as recently shown, KDP crystals may adsorb various organic dyes.

Dye inclusion crystals have been successfully used in a wide range of areas, including solid-state lasers, room-temperature phosphorescence etc. For example, dyed crystals have been fashioned into new kinds of laser gain media and used in the development of new crystals with predetermined physical properties. Very interesting are also those crystals which properties can be modified by introducing various kinds of additions and impurities. Thereat, it is possible not only to change practically significant crystal characteristics but also to create new properties, which do not manifest themselves in the pure crystals [1]. During the past few years there have been reported developments of very complex combinations of inorganic crystal matrixes with organic impurities. Such developments are greatly promising from the viewpoint of the growth of dye inclusion crystals (DICs) and creation of solid-state dye lasers (SSDL) on their base [2−4]. Therefore, investigation of regularities in the interaction of organic impurities with the matrix and elucidation of the mechanism of dye incorporation into the crystal are topical problems of the considered direction of functional materials research.

This paper presents the results concerning the growth and comprehensive investigations of the properties of KDP crystals doped with the organic dye *Xylenol Orange (XO)*.

The investigation was performed on the crystals of potassium dihydrogen phosphate (KDP) with *XO*. As a starting material for the growth of the crystals, there was used the salt containing the main crystal-active impurities on the level of $10^{-5}-10^{-4}$ mass.%. The typical transparent KDP single crystals measuring up to $10\times10\times12$ mm^3 and $80\times80\times80$ mm^3 were grown by the method of solvent evaporation at room temperature under the conditions of natural convection and by the method of temperature decrease, respectively (Fig. 1). Thereat, the growth rate varied from 1 mm/day to 5 mm/day depending on the growth conditions. Experimental conditions provided free crystal growth in **x**, **y**, **z** directions. While choosing the dyes the following criteria were used: sufficient solubility; the absence of chemical interaction with the main substance; dyeing of the crystal in the bulk.

On the base of preliminary studies there was chosen *Xylenol Orange (XO)*, triphenilmetane dye of sulphonephthalein range (Fig. 1). The dye concentration in the solu-
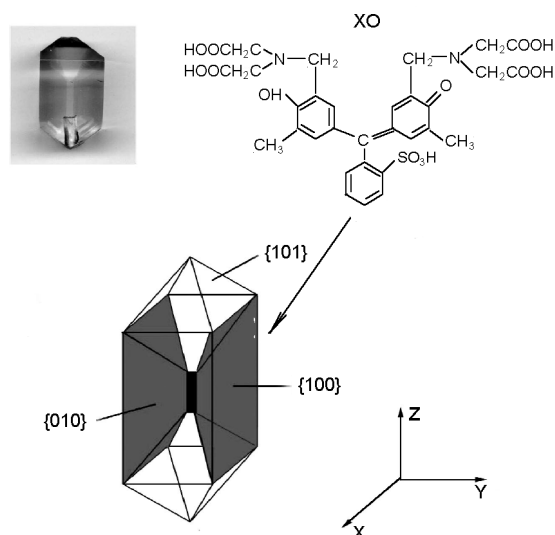

Fig. 1. Structure of *Xylenol Orange* (*XO*) and KDP crystal grown in the presence of *XO*.

tion varied within the limits from 200 to 4000 ppm. The content of *XO* in the crystals was determined by comparing the absorption spectra of aqueous solutions of the samples and the solutions with known dye content. For the measurements, the samples with the same size of $8\times8\times8$ mm^3 were cut from KDP + *XO* crystal strictly oriented along the crystallographic axes.

The optical transmission spectra of the solutions and the crystals from UV to IR in the wavelength range of 200−1100 nm were registered by means of a SF-56 (LOMO) recording spectrophotometer at room temperature using the conventional two-beam technique with respect to air, disregarding the loss by Fresnel reflection.

The excitation and emission luminescence spectra of XO-containing KDP crystals were measured on a "Hitachi F4010" fluorimeter in the region of 350−700 nm. As an excitation source, there was used a nitrogen laser ($\lambda = 337$ nm). The polarization characteristics of KDP + *XO* crystals were investigated using a unit which comprised a halogen lump with lens and diaphragm, rotating polarizer and radiation receiver ILD-2M.

To determine the degree of radiation hardness of the dye inclusion crystals, the effect of irradiation on the optical absorption of the crystals was investigated. ^{60}Co radioactive isotope served as a source of γ-rays.

The laser damage threshold was measured using Nd:YAG laser along **x** and **y** crystal axes ($\lambda = 1064$ nm, $\tau = 10$ ns and pulse

energy up to 4 mJ, focus length f = 5 cm, focus area $1.58 \cdot 10^{-5}$ cm^2). In the way of 1-on-1, usually 90 positions of the sample were irradiated at the same energy. The break-down was registered visually from residual destruction observed at illumination using He-Ne-laser radiation (632.8 nm) with a lower power (30 mW). In the performed experiments, the maximum density of the energy of the radiation transmitted through the sample without its destruction was assumed to be the threshold of bulk laser damage (BLD).

Dyeing of KDP crystals. Earlier for the growth of dyed KDP crystals there were used such dyes as Chicago Sky Blue [2, 5], Amaranth [2, 5–7], Sunset Yellow [5, 7], Trypan Blue [5], Direct Blue [2, 8], Fast Red Extra [5, 8], stilbene [5] etc. However, practically in all the cases, with the exception of hematein dye [3], only the pyramidal growth sector {100} turned out to be colored, whereas the prismatic sector {100} remained transparent. In the opinion of the authors [1], such a phenomenon is caused by the electrostatic interaction of the dye anions with the positively charged face {100}.

Using *XO* we obtained the colored prism {100} and the uncolored pyramid {101}. Such a result agrees with the structure of this compound (Fig. 1). It is interesting to note that multiple increase of the dye concentration in the solution (up to 4000 ppm) practically does not result in its increase in the crystals. In particular, the dyed {100} and {101} sectors contain 6–10 ppm and 0.6 ppm (that is comparable with determination error) of the dye, respectively.

Habit modification of dyed KDP crystals. As is known, the shape of KDP crystal is a combination of tetragonal prism and dipyramid with the lattice parameters $\mathbf{a} = \mathbf{b}$ = 7.458Å, $\mathbf{c}$ = 6.991Å [9], the faces {100} and {010} being completely identical, i.e. the ratio $\mathbf{x:y}$ = 1 (see Fig. 1). The theoretical investigation performed in [10] shows that incorporation of the dye into the crystal lattice of the matrix (KDP + *Amaranth*) may be accompanied with a change of the elementary cell parameters and a shift in the basal plane.

While using *XO* as an addition we were the first to reveal a violation of the ratio $\mathbf{x:y}$. Thereat, with increasing contents of the dyes in the solution the deviation of $\mathbf{x:y}$ ratio from 1 also increases and reaches 20 % at the maximum concentrations. Our X-ray examinations show that in this case the parameters $\mathbf{a}$ and $\mathbf{b}$ remain unchanged.

At the same time, the diffraction patterns obtained for the dyed crystals are characterized by the presence of additional X-ray reflexes which can hardly be identified. Such a change of the crystal morphology seems to be bound up with essential local distortions which arise due to the incorporation of organic macromolecules into the matrix crystal lattice and, consequently, with the formation of elastic domains. However, the final conclusion concerning the said problem requires an additional study.

Coloration of dyed KDP as a function of pH. As is known, *XO* is an acid-base indicator. In this connection, coloration of the mother solutions (and, consequently, of the crystals) at different values of acidity is defined by the presence of different forms of indicator depending on dissociation of the latter. In particular, at pH = 2.1 *XO* is contained in the solution in the molecular (non-dissociated) form, the solution is pink, whereas the grown crystals are practically colorless ($C_{XOcryst.}$ = 0.6 ppm).

The increase of pH leads to a stepwise deprotonization of *XO* molecule; at pH = 4.1 the crystals acquire orange-pink color ($C_{XOcryst.}$ = 5.5–9.5 ppm), at pH = 5.6 they become pinkish-violet ($C_{XOcryst.}$ = 5.1 ppm). It should be noted that for all the values of acidity the ratio $\mathbf{x:y}$ is also different from 1. So, the character of the incorporation of organic molecules into the crystals and their coloration are defined by the form in which the dye is present in the solution.

Spectroscopic investigations. Due to their optical characteristics, KDP crystals are irreplaceable materials for quantum electronics and non-linear optics. They are practically transparent in the visible and near infrared region of the spectrum. The crystals' edge of fundamental absorption in the UV-region corresponds to ~200 nm [11], however, some samples have noticeable absorption bands at 215 and 270 nm. This is bound up with the impurity composition of the crystals and with the presence of structure defects in them. Shown in Fig. 2 are the transmission spectra of KH$_2$PO$_4$ solutions and KDP crystals, both pure and containing *XO* additions. The spectra corresponding to the pure samples have no peculiarities and are typical of the solutions and crystals with high degree of purity and optical perfection. Thereat, the transmission spectra of the undoped crystals in the directions $\mathbf{x}$ and $\mathbf{y}$ are absolutely identical.

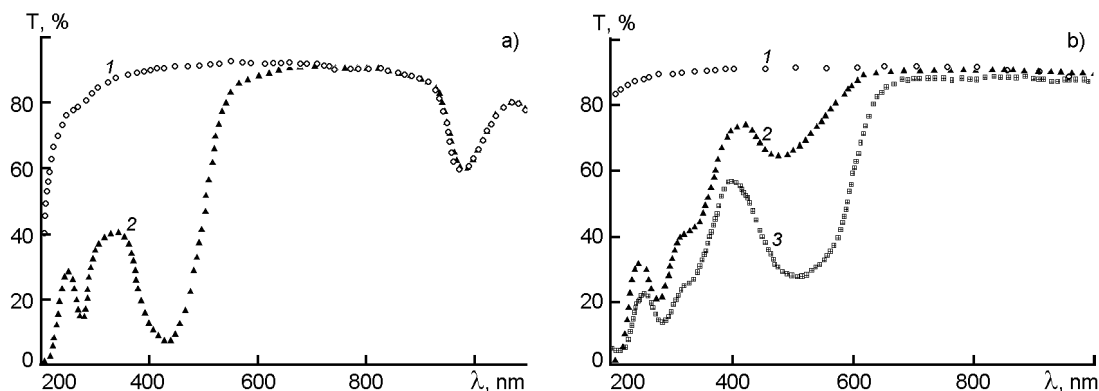The absorption bands characteristic of the doped solutions (Fig. 2a) and crystals

Fig. 2. Transmission spectra of KH_2PO_4 solutions and KDP crystals ({100} face): a) *1* — pure solution, *2* — KH_2PO_4 + *XO* solution; C_{XO} = 30 ppm; b) *1* — KDP crystal without dye, *2* — KDP + *XO*, $C_{XO\ cryst.}$ = 5.5 ppm, pH = 4.1, *3* — KDP + *XO*, C_{XO} *cryst.* = 5.1 ppm, pH = 5.6.

(Fig. 2b) lie within the wavelength range from 200 to 600 nm. Comparison of these spectra shows that while passing from the solutions to the crystals the bands at 270 and 435 nm are shifted towards longer wavelengths; for "alkaline" crystals this effect is more vivid (275 and 470 nm at pH = 4.1; 290 and 505 nm at pH = 5.6). In our opinion, this is caused by different forms of the presence of the dye in the liquid or solid matrix.

Transmission anisotropy. As noted above, the transmission spectra of the pure crystals in the directions **x** and **y** are identical. For KDP + *XO* crystals the transmission in the directions **x** and **y** essentially differs (Fig. 3), i.e. there takes place transmission anisotropy. In our opinion, this is bound up with different orientation of the dye particles in the process of interaction with different crystal faces.

It is found that due to the incorporation of the organic dye into the crystal the latter acquires pronounced dichroic properties. This is caused by the fact that the dye particles occupy different fixed positions with respect to the crystallographic axes. Fig. 4a shows the intensity I/I_0 of blue-green polarized light passing through the crystal depending on the angle θ between the plane of vibration and the crystallographic axis **z** (the electric vector **E** rotates in the plane **xz** of the crystal). The dependence is described by the following equation:

$$I = I_0 + I_1\cos^2\theta,$$

where I_0 and I_1 are constant values. The minimum and the maximum of light absorption are observed when **E** ‖**z** and **E**⊥**z**, respectively.

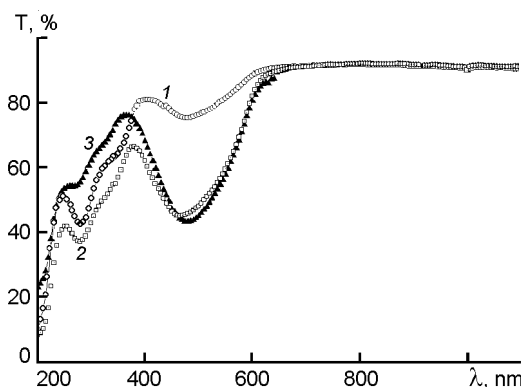The optical spectrum of KDP + *XO* is highly dichroic. The spectral characteristics

Fig. 3. Transmission spectra of KDP + *XO* crystals in the directions **x** (*2*), **y** (*1*), **z** (*3*).

presented in Fig. 4b show dichroism of the absorption spectra of KDP + *XO* crystals in polarized light for three crystallographic directions. As seen from the figure, manifestation of dichroism in the doped crystals depends on the orientation (such a fact has been earlier noted for the absorption spectra obtained in non-polarized light).

Investigation of luminescence shows that *XO* does not emit in water and in aqueous solutions of KH_2PO_4. Luminescence appears only after the dye incorporation into the crystal. Presented in Fig. 5 are the spectra of luminescence (2) and luminescence excitation (1) measured in 370–670 nm wavelength region.

The maximum value of the luminescence excitation intensity is observed at λ = 502 nm, the luminescence maximum corresponds to λ = 602 nm. So, the Stock's shift is equal to 100 nm (3300 cm⁻¹). The width of the optical absorption band is $\Delta\lambda_{0.5}$ ~ 80 nm (2300 cm⁻¹). It should be emphasized that for the pure crystals luminescence at room temperature is absent.
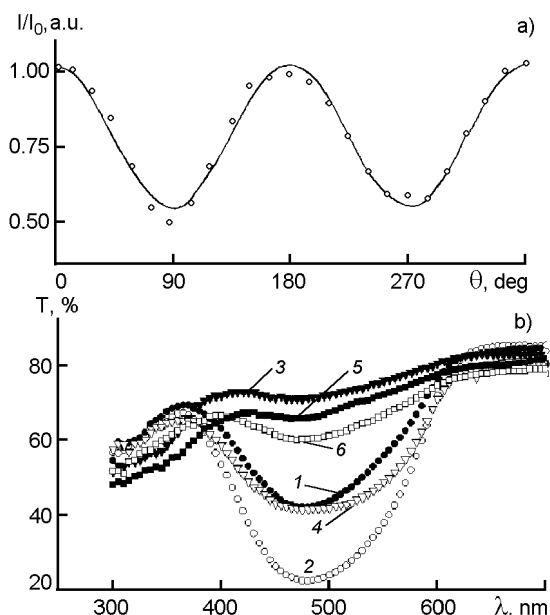
Fig. 4. a) Polarization characteristics of KDP + *XO* crystal; b) Absorption spectra of KDP + *XO* depending on polarization of incident radiation in the directions: **z** (*1* — φ = 0°, *2* — φ = 90°), **x** (*3* — φ = 0°, *4* — φ = 90°), **y** (*5* — φ = 0°0, *6* — φ = 90°0).

In KDP + *XO* crystals luminescence is highly polarized. Excitation of luminescence by nitrogen laser along the crystallographic axis **x(y)** and registration of the emitted light passing through polarizer along the axis **y(x)** show that the emitted light maximum is observed in the case when the transmission axis of the polarizer is parallel to the axis **x(y)**. The emitted light minimum is observed if the polarizer is parallel to the direction **z**.

Experimental studies of the action of γ-irradiation on the dyed crystals allow to establish that destruction of the dye in the crystals is initiated at a dose of $3 \cdot 10^2$ Gy. After the action of $2.7 \cdot 10^3$ Gy irradiation the optical spectra of the samples are practically similar to those of the nominally pure crystals.

Measurements of laser strength in KDP + *XO* crystals for different crystallographic directions show that the value of BLD threshold is 36 J/cm² and 28 J/cm² at irradiation of the crystal in the direction parallel and perpendicular to the optical axis, respectively. The obtained data are close to the values of BLD threshold in the pure crystal, and this is obviously caused by the absence of the dye absorption bands at the irradiation wavelength (1064 nm).

As established in the course of the performed investigations, *Xylenol Orange* (*XO*)
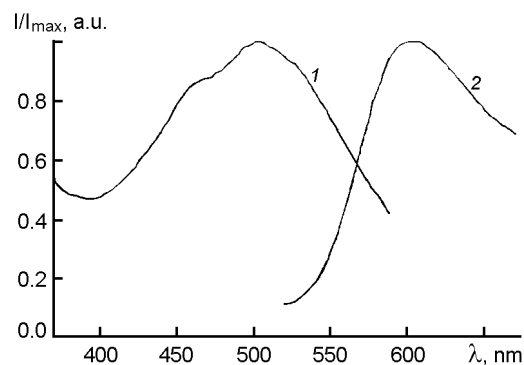

Fig. 5. Excitation (*1*) and emission (*2*) luminescence spectra of KDP + *XO* crystal.

preferentially dyes the faces {100} and {010} of KDP crystal. The introduction of the organic dye into the crystal matrix of KDP leads to changes in the crystal's habit and to the appearance of absorption anisotropy (λ = 475 nm) along the axes **x** and **y**. In the dyed crystals there is revealed luminescence at room temperature, which is absent for the dye, its aqueous solutions and pure KDP. KDP + *XO* crystals are characterized by dichroism which depends on the orientation. The damage threshold of the doped crystals is shown to be of the same order of magnitude as that for the pure crystals.

Finally, it should be noted that the use of the considered material in practice requires further theoretical and experimental investigations. The authors are grateful to Nikolov O.T. for the performed experiments with γ-irradiation of the samples.

References

1. B.Helczer, *Key Engineering Mat.*, **101−192**, 95 (1995).
2. J.Anand, S.Jang, B.Kahr, *Ferroelectrics*, **191**, 293 (1997).
3. B.Kahr, R.W.Gurney, *Dyeing Crystals, Chem. Rev.*, **101**, 893 (2001).
4. B.Kahr, private communication (2003).
5. J.A.Subramony, Ph.D.Dissertation, Purdue University (1999).
6. N.Zaitseva, L.Carman, I.Smolsky et al., *J. Cryst. Growth*, **204**, 512 (1999).
7. S.Hirota, H.Miki, K.Fukui et al., *J. Cryst. Growth*, **235**, 541(2002).
8. B.Kahr, S.H.Jang, J.A.Subramony et al., *Adv. Mater.*, **8**, 941 (1996).
9. G.Ravy, A.S.Haja Hameed, P.Ramasamy, *J. Cryst. Growth*, **207**, 319 (1999).
10. S.V.Grabovsky, I.V.Shnaidshtein, B.A.Strukov, *Rus. Solid State Phys.*, **45**, 518 (2003).
11. D.Eimerl, *Ferroelectrics*, **72**, 95 (1987).

Вплив органічного барвника на вирощування та оптичні властивості KDP

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Вирощено кристали KDP з домішками органічного барвника *Xylenol Orange* (*XO*). Показано, що *XO* переважно забарвлює грані {100} і {010} кристала; вміст барвника в кристалі практично не залежить від його концентрації у розчині. Виявлено зміну габітусу кристалів, що вирощені у присутності барвника: відношення розмірів граней {100} і {010} (**x** і **y**) при максимальних концентраціях *XO* досягає 1,2. Вивчено вплив кислотності розчину на характер забарвлення кристала. Установлено, що в залежності від pH розчину змінюються як колір, так і інтенсивність забарвлення. Виміряно спектри пропускання розчинів і кристалів KDP + *XO* у діапазоні довжин хвиль 200−600 нм. Виявлено анізотропію пропускання у напрямках **x** і **y** для забарвлених кристалів. Показано, що дихроїзм у KDP + *XO* є орієнтаційно залежним. Виміряно спектри збудження та люмінесценції забарвлених кристалів. Визначено величину порога об'ємного лазерного руйнування. Обговорюється механізм входження органічного барвника у кристалічну матрицю.