

The effect of thermal annealing on linear and nonlinear optical response of dyed KDP crystals

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Potassium Dihydrogen Phosphate crystals (KDP) doped with the organic Xylenol Orange (XO) dye are grown, the XO concentration in the crystal matrix is about 10 ppm. The spectral and luminescent properties of nominally pure, dye-doped and the dye-doped/annealed at 150°C crystals (KDP, KDP:XO and KDP:XO_{an}) are measured. The annealing temperature effect on the degree of dye protonation in the crystal matrix is established. Analysis of the IR-absorption spectra reveals a strong interaction between the incorporated dye molecules and the hydrogen subsystem of the matrix. The nonlinear optical (NLO) properties of KDP, KDP:XO and KDP:XO_{an} crystals are studied within the self-action effect of picosecond laser pulses at 532 nm. The mechanism of photoinduced bleaching and the effects of laser beam self-focusing (in KDP) and self-defocusing (in KDP:XO and KDP:XO_{an}) are supposed to be due to resonance excitation of the subsystems of intrinsic defects and dye molecules, correspondingly. For KDP:XO_{an} it is shown thermal annealing of intrinsic crystal defects leads to domination of more effective NLO response of the subsystem of dye molecules that is correlated with photoluminescence data.

Выращены кристаллы дигидрофосфата калия, допированные красителем ксиленоловым оранжевым (КО), концентрация КО в матрице кристалла порядка 10 ppm. Измерены спектральные и люминесцентные свойства номинально чистого и допированного кристаллов, а также допированного кристалла, отожженного при 150°C (KDP, KDP:КО и KDP:КО_{от.ж.}). Установлено влияние температуры отжига на степень протонирования красителя в кристаллической матрице. Анализ ИК-спектра поглощения свидетельствует о сильном взаимодействии молекул красителя с протонной подсистемой матрицы. Изучены нелинейно-оптические (НЛО) свойства KDP, KDP:КО и KDP:КО_{от.ж.} кристаллов при самовоздействии пикосекундных лазерных импульсов на 532 нм. Предполагается, что механизм фотоиндуцированного просветления и эффекты самофокусировки (в KDP) и дефокусировки (в KDP:КО и KDP:КО_{от.ж.}) обусловлены резонансным возбуждением подсистемы внутренних дефектов и подсистемы молекул красителя соответственно. Показано, что в KDP:КО_{от.ж.} термоотжиг дефектов приводит к доминированию более эффективного НЛО отклика подсистемы молекул красителя, что коррелирует с данными фотолюминесценции.

Nonlinear optical (NLO) crystals, in particular, potassium dihydrogen phosphate crystals (KDP, KH₂PO₄), are widely used for frequency conversion and optical switching in modern optoelectronics and photonics [1].

Moreover, these crystals are successfully used as a model system for studying the mechanism of crystal growth from the solution, as well as for finding out a relation between nonlinear optical properties and

crystal structure. It is widely discussed in the literature the possibility to create new NLO media based on complex combinations of water-soluble inorganic matrices with organic impurities [2]. Special emphasis is laid on the development of solid state dye lasers in which laser radiation conversion and subsequent pumping of organic dye are realized in the same medium [3–6]. The dyes absorb in the range of 500–550 nm, thus the second harmonic generation of Nd:YAG laser light (532 nm) is suitable for pumping the dyes incorporated in the host crystal in order to achieve lasing effect.

As shown in [7–9] KDP crystals can absorb a variety of organic molecules, such as Chicago Sky Blue, Amaranth, Sunset Yellow, Trypan Blue, Direct Blue, Stilbene, Xylenol Orange, Methylthymol Blue etc. In our previous paper [9] experimental results were presented and discussed concerning the influence of organic dyes such as Xylenol Orange and Methylthymol Blue on the growth kinetics, habit modification and coloration of KDP single crystals, as well as the effect of external factors, e.g. UV- and γ -irradiation on the optical properties of dye-doped KDP crystals.

Xylenol orange (XO) — 3,3'-bis[N,N-di(carboxymethyl)aminomethyl]-*o*-cresolsulfonephthalein is a water-soluble dye of triphenylmethane group used as pH indicator. Whereas XO forms stable complexes with a number of transition metals, it is widely used in analytical chemistry [10] and in radiation dosimeters [11].

Thus, it may be stated that KDP crystals doped with organic molecules such as Xylenol Orange have the potential for combining high optical nonlinearity and chemical flexibility of organic dyes with time and thermal stability, excellent transmittance and the optical nonlinearity of inorganic matrix necessary for the creation of new nonlinear optical media.

In this study the results of comprehensive investigation of the influence of thermal annealing on the spectral and nonlinear optical properties of KDP single crystals doped with Xylenol Orange dye are presented.

Pure and dye-doped KDP crystals were grown by the method of temperature lowering (see details at [9]). The dye-doped KDP crystals had the dimensions $80 \times 80 \times 80$ mm³ (Fig. 1).

The content of XO in the crystals was determined by comparing the absorption spectra of the samples and of the solutions



Fig. 1. As grown KDP single crystal doped with Xylenol orange dye.

with known dye contents. The dye concentration in the growth solution was 500 ppm. We obtained colored prismatic {100} sectors and transparent uncolored pyramidal {101} sectors with XO concentration in the crystal of about 10 ppm.

The absorption spectra of pure and dye-doped KDP crystals were measured in 200–1100 nm wavelength region using UV-vis-NIR spectrophotometer (Lambda 40, Perkin Elmer), for IR-measurements (4000–400 cm⁻¹ range) Fourier spectrometer of Perkin Elmer Spectrum One type was used (the samples were mixed with KBr and pressed into pellets). Photoluminescence measurements were carried out on a spectrophotometer model SDL-2 (LOMO).

The self-action effect of mode-locked Nd:YAG laser second harmonic radiation (532 nm) in the crystals was studied by spatial beam profile distortions analysis in the far field [12]. The normal incidence direction of laser beam towards the crystals interface does not correspond to phase matching condition for harmonics generation, thus we can omit the contribution of the quadric NLO response. We recorded simultaneously the total transmittance of the samples and the on-axis transmittance in the far field, dealing with the photoinduced absorption and the nonlinear refraction index variation, versus the peak intensity of 30 ps (FWHM) laser pulses. We were working in single pulse extraction regime with 5 Hz repetition rate. In order to measure NLO response in moderate intensity range up to 15 MW/cm² with high signal-to-noise ratio the samples were positioned at the distance 22 cm from the focusing lens (focal length 11 cm) far beyond the

Table 1. Samples characterization: thickness d , optical absorption coefficient α at 532 nm, XO dye concentration n_D and the laser intensities I_p and I_s corresponding to the peak of the photoinduced transparency (maximum) and to the photobleaching saturation threshold (minimum) of the total transmittance variation dependencies presented at Fig. 5a and Fig. 6a

Sample	d , mm	α , cm^{-1}	n_D , cm^{-3}	I_p , MW/cm^2	I_s , MW/cm^2
KDP	0.86	0.004	–	1.5	4.4
KDP:XO	0.79	13.2	10^{17}	3.8	7.5*
KDP:XO _{an}	0.79	10.8	10^{17}	1.6	3.0

beam waist region. The intensity was controlled with neutral graded attenuator that did not deflect the beam. The crystals were illuminated with diverging beam with gaussian profile of about 0.5 mm (FWHM) diameter at the sample plane. The on-axis (or closed aperture) transmittance through 1 mm radius diaphragm was registered at the distance 56.5 cm from the focusing lens.

In the NLO experiments we have studied thin polished crystalline plates with 10×10 mm cross-section (Z cut, prism), their thicknesses d was about 0.8 mm (see Table 1).

The samples meant for absorption and photoluminescence investigations were manufactured in the form of $10 \times 10 \times 10$ mm³ cubes with optically polished faces oriented along the crystallographic axes.

All the experimental samples were cut out of the colored prism growth sector {100} and annealed in air at a temperature up to 150°C.

At room temperature the absorption spectrum of XO-doped KDP crystals (KDP:XO) in 200–700 nm wavelength range has three broad absorption bands at 280, 340 and 475 nm caused by the presence of the dye [9]. As seen from Fig. 2a, the band with $\lambda_{max} = 475$ nm has a complex structure and can be approximated by the resolution of the basic curve into two Gaussians: G_1 (with $\lambda_{max} = 475$ nm, the half-width ~ 117 nm, the integral area under the curve ~ 126) and G_2 (with $\lambda_{max} = 570$ nm, the half-width ~ 41 nm, the integral area under the curve ~ 9). Annealing of the doped samples at temperatures up to 150°C is not accompanied with destruction of the dye. Meanwhile, heating of the sample gives rise to redistribution of the intensity in the bands G_1 (with $\lambda_{max} = 522$ nm, the half-width ~ 95 nm, the integral area under the curve ~ 36) and G_2 (with $\lambda_{max} = 575$ nm, the half-width ~ 33 nm, the integral area under the curve ~ 17). Moreover, under such condi-

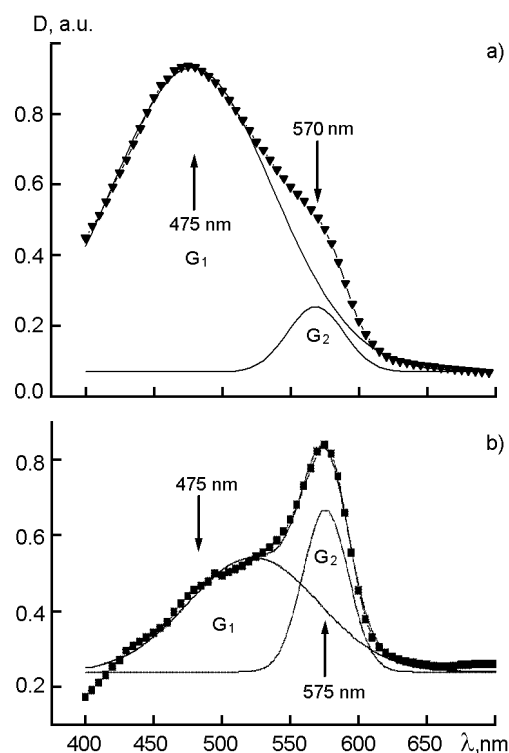


Fig. 2. Absorption spectra of KDP:XO crystal in the region of singlet-singlet transition at 25°C (a) and of the sample annealed at 150°C (b).

tions the ratio of the integral Gaussian areas essentially changes: $S_{G1}:S_{G2} = 14:1$ (KDP:XO sample prior to annealing), $S_{G1}:S_{G2} = 2:1$ (KDP:XO after annealing). The color of the annealed KDP:XO samples changes from yellow-red to purple-red.

Xylenol Orange has 10 possible ionic forms in aqueous solution. The pH factor controls which of these forms are present in solutions and their partial concentration. It is known that the dye is present in the solution (pH = 4.1) in two molecular forms [13] H_3XO^{3-} and H_2XO^{4-} . The dominating form of the dye is H_3XO^{3-} which manifests itself in the main absorption peak at $\lambda_{max} = 475$ nm (G_1) in the spectrum shown in Fig. 2a. The presence of the dye in the form H_2XO^{4-}

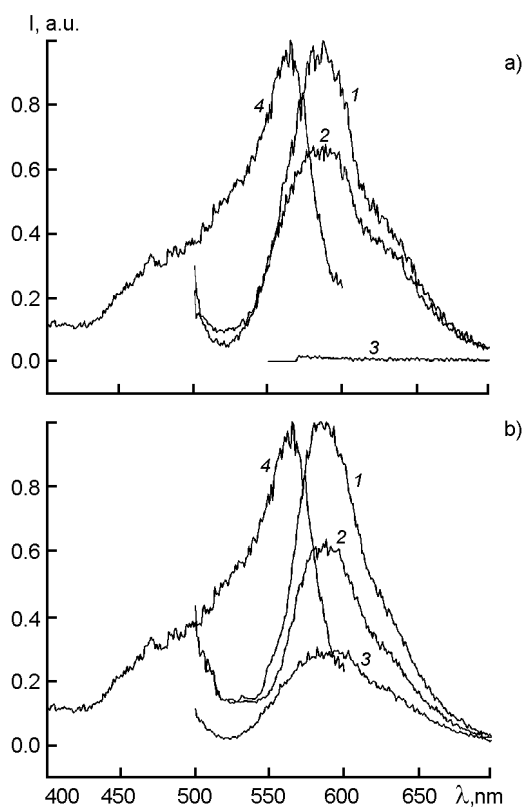


Fig. 3. (a) Photoluminescence spectra with different excitation wavelength of KDP:XO 550 nm (1), 490 nm (2) and of pure KDP crystal — 490 nm (3); PL excitation spectrum of KDP:XO crystal with monitor at 550 nm (4); (b) KDP:XO_{an} PL spectra with excitation wavelength 550 nm (1), 530 nm (2), 490 nm (3) and PL excitation spectrum with monitor at 630 nm (4). Sample before (a) and after annealing at 150°C (b).

corresponds to the features of the long-wavelength region of the band with $\lambda_{max} = 575$ nm (G_2). Analysis of the structure of the absorption band in the region of singlet transition for the annealed samples reveals that the annealing of the crystals leads to redistribution of the integral area values for G_1 and G_2 responsible for the change of the relative concentration of the dye in different molecular forms (Fig. 2b) — the concentration of H_3XO^{3-} (G_1 band) diminishes, whereas the concentration of H_2XO^{4-} (G_2 band) considerably increases. Thus, the observed transformation of the spectrum testifies to the fact that the annealing of KDP:XO crystals changes the molecular form of the dye: $H_3XO^{3-} \rightarrow H_2XO^{4-}$. This is analogous to the effect of the pH factor change of for aqueous XO solution [9].

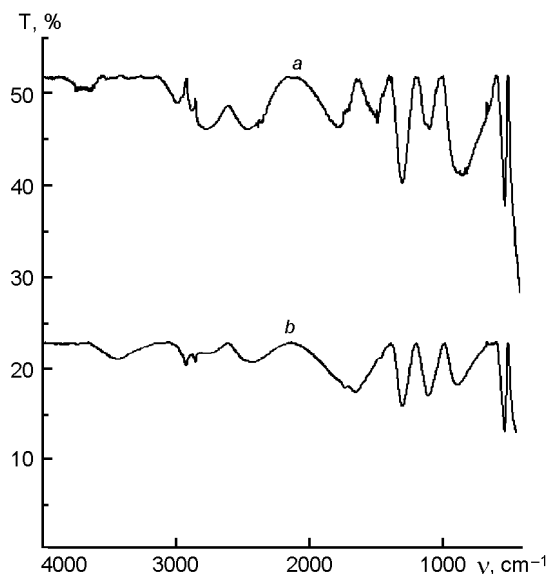


Fig. 4. FTIR spectra of pure KDP (a) and KDP:XO samples (b).

The excitation and photoluminescence (PL) spectra of the samples of nominally pure KDP, dye-doped KDP crystals which did not undergo thermal treatment and dye-doped KDP crystals subjected to thermal annealing at 150°C, were investigated in 400–700 nm wavelength region. The obtained data are presented in Fig. 3a, b. The excitation and photoluminescence spectra of non-annealed and annealed KDP:XO crystals are practically identical. Thereat, for $\lambda_{max} \sim 570$ nm the excitation spectra of both samples coincide with the absorption band which corresponds to the dye in the molecular form H_2XO^{4-} : $\lambda_{max} = 575$ nm. The measurements of PL performed while shifting the excitation wavelength towards the short-wave range of the spectra show that the luminescence intensity diminishes. This confirms the fact that the main contribution to luminescence belongs to the absorption center H_2XO^{4-} .

FTIR spectral analysis of KDP:XO single crystals was carried out in the medium infrared region extending from 400 to 4000 cm^{-1} . The spectrum is shown in Figure 4. The presented IR absorption spectrum of pure KDP crystal is unambiguously interpreted and coincides with known literature data [14–16]. In the IR-spectrum of KDP:XO crystal the vibration connected with free OH stretching, which reveals at 3600 cm^{-1} in pure KDP [17], is absent, and this fact obviously testifies to a strong interaction between Xylenol Orange molecules

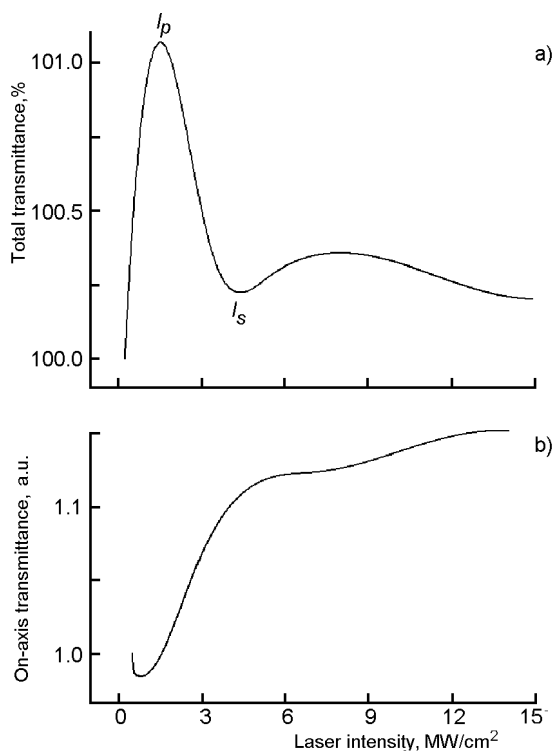


Fig. 5. The total transmittance (a) and on-axis transmittance (b) of pure KDP crystal normalized on linear transmittance T_{lin} versus the peak laser intensity at 532 nm (reference — air).

with OH groups. The absorption at 3441 cm^{-1} in the doped crystals may be attributed to hydrogen bonded OH stretching. It is to be noted that there are observed essential changes for the absorption region of the combination bands ($1500\text{--}1700\text{ cm}^{-1}$), in particular, KDP:XO crystal has a broad band with a maximum at 1657 cm^{-1} which corresponds to the asymmetrical and symmetrical vibrations (COO^-) (1632 and 1400 cm^{-1} , respectively).

Significant data for characterization of the subsystem of organic dye molecules incorporated into KDP crystal matrix may be obtained while studying the NLO response at the self-action of picosecond laser radiation pulses of the second harmonic of Nd:YAG laser. Such an approach proved to be effective for the investigation of NLO properties of low-dimensional subsystems in complex heterogeneous systems of both inorganic [18] and organic [19] origin.

The NLO response of the KDP crystal with respect to air was used as a reference standard for establishing the partial contribution of the NLO properties of the organic dye subsystem in the crystalline matrix. The total transmittance of the pure KDP

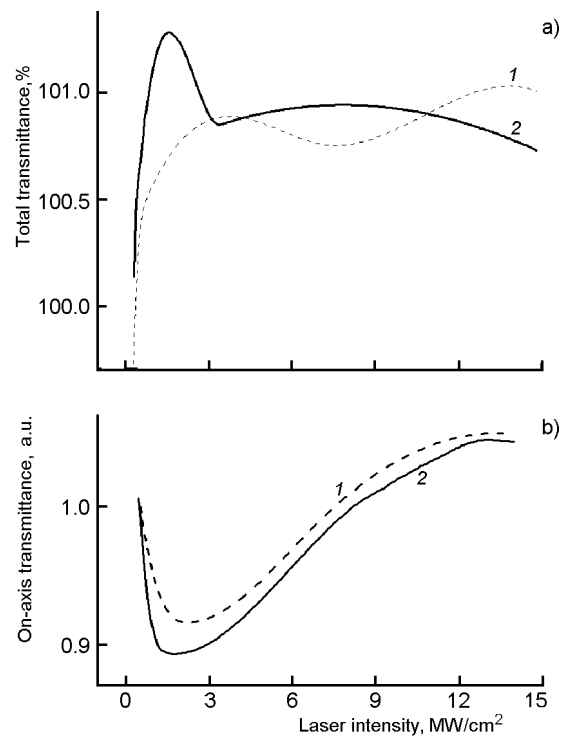


Fig. 6. The normalized total transmittance (a) and the normalized on-axis transmittance in the far field (b) versus the peak laser intensity at 532 nm of KDP:XO — 1, and KDP:XO_{an} — 2 (reference — corresponding NLO response of the pure KDP presented at Fig. 5).

and on-axis transmittance in the far field versus the peak laser intensity are presented at Fig. 5(a,b). Fig. 6(a,b) characterize the total transmittance and the on-axis transmittance in the far field in doped KDP:XO and KDP:XO_{an} normalized on the corresponding dependences of the NLO response of pure KDP crystals accordingly.

To eliminate the contribution of photoinduced processes of bleaching/darkening while estimating the refractive response of the medium, the experimental dependences of the on-axis transmittance in the far field were normalized to the corresponding dependences of the total transmittance coefficient on the intensity of incident laser radiation [20] presented in Fig. 5a, Fig. 6a and all of curves were normalized to the transmittance at low intensity levels in the used registration geometry to reveal the contribution of photoinduced variations.

Photoinduced changes of the crystals' transmittance accompanying the rise of laser radiation intensity (Fig. 5, 6a) allow to estimate the changes in the imaginary part of the cubic NLO susceptibility $\text{Im}(\chi^{(3)})$ [12]. Analysis of the on-axis transmittance

Table 2. Real and imaginary parts of the cubic nonlinear optical susceptibility $\chi^{(3)}$ for the crystal samples at the photobleaching ($I \leq I_p$) and the photobleaching saturation ($I_p < I \leq I_s$) ranges of the peak laser intensities at 532 nm

Sample	Reference	$I \leq I_p$		$I_p < I \leq I_s$	
		$\text{Re}(\chi^{(3)}), 10^{-9}$ esu	$\text{Im}(\chi^{(3)}), 10^{-9}$ esu	$\text{Re}(\chi^{(3)}), 10^{-10}$ esu	$\text{Im}(\chi^{(3)}), 10^{-10}$ esu
KDP	air	0.8	-1.1	31.4	8.5
KDP:XO	KDP	-6.5	-0.5	8.1	-0.9
KDP:XO _{an}	KDP	-11.0	-1.4	10.5	6.1

in the far field (Fig. 5, 6b) makes it possible to estimate NLO coefficient of the refractive index, as well as the real part of the cubic NLO susceptibility $\text{Re}(\chi^{(3)})$ [18].

All the samples showed the effect of photoinduced bleaching which reaches its maximum at the intensity I_p (Fig. 5, 6a) at the initial stage. At the intensity I_p (see Table 1) the total transmittance has its maximum $T(I_p)$ and at $I < I_p$ the negative values of the coefficient $\text{Im}(\chi^{(3)}) < 0$, the efficiency of photo-induced bleaching makes $\sim 1\%$ of the value of linear transmittance T_{lin} (Fig. 5, 6b).

At the next interval of the increases the radiation intensity at $I_p < I < I_s$ (see Table 2) leads to decrease of the total transmission (to differential darkening) of the samples: $\text{Im}(\chi^{(3)}) > 0$ provided that $T(I) > T_{lin}$. The energy of the local minimum of the total transmittance $T(I_s)$ corresponds to the threshold saturation intensity I_s ("switch-off") of the primary mechanism of photoinduced bleaching.

I_p and I_s values for the dye subsystem in non-annealed KDP:XO crystal (Table 1) essentially differ from the corresponding values obtained for KDP and KDP:XO_{an} crystals ($I_p(\text{KDP:XO}) \geq I_s(\text{KDP:XO}_{an})$). Such an approach is explained by the fact that in non-annealed KDP:XO the NLO response is formed by the competitive contributions of the defect subsystem of KDP crystal matrix and the dye subsystem, as it takes place in KDP:XO_{an} with reduced defect subsystem of the crystal matrix. That is why, the observed intensity values of the characteristic photoinduced changes are considerably shifted with respect to the corresponding values of the said subsystems.

After saturation of the processes of photo-induced bleaching of the dye molecules in KDP:XO_{an}, the dependences of the total transmittance for both crystals (Fig. 6, $I > I_s$) practically coincide.

Laser beam self-focusing in the crystal is observed in the form of the increase of the

on-axis transmittance accompanied with the effect of photoinduced rise of the transmittance value of about 1 % in KDP at $I \leq I_p$ (Fig. 5b). The total transmittance of KDP reaches 92.2 % in the maximum of photoinduced bleaching (at $I = I_s$).

The expected values of imaginary $\text{Im}(\chi^{(3)}) = -1.1 \cdot 10^{-9}$ esu and parts $\text{Re}(\chi^{(3)}) = 8 \cdot 10^{-10}$ esu calculated at KDP excitation in the region of bleaching ($I < I_p$) are by four orders of magnitude higher than the values of the real component of the cubic NLO susceptibility obtained by other authors [21, 22] at higher excitation intensities.

The observed effect is based on the resonance excitation of the intrinsic and photoinduced defects located in the band gap of the KDP crystal. Transient optical absorption of hole polarons is experimentally investigated in [23], electronic structure calculations of intrinsic and extrinsic hydrogen point defects in KDP are presented in [24].

The optical absorption of the subsystem of KDP crystal defects and the subsystem of dye molecules in KDP:XO_{an} crystals diminishes under the action of pulsed laser radiation with 532 nm wavelength (2.33 eV) in a narrow intensity range $I < I_s = 4.4/3.0$ MW/cm² with the maximum $I_p = 1.5/1.6$ MW/cm² (see Table 2). At higher excitation levels $I > I_s$ the NLO response efficiency decreases essentially and leads to small variations of the coefficients of total and on-axis transmittance in the far field.

The wavelength of laser excitation corresponds to the resonance excitation in the overlap of the two broad bands of dye absorption: at 575 nm (2.16 eV) and 474 nm (2.61 eV) for the subsystem of the dye molecules in KDP:XO_{an}. Similar effect of excitation in the overlap of the wide bands at 588 nm (2.11 eV) and 492 nm (2.52 eV) [23] bound up with defect states, is also observed in KDP crystal. The estimation made in [23] for the concentration of optical absorption centers in KDP at 2.2 eV (564 nm) which is equal to 10^{17} cm⁻³ corre-

sponds to the concentration of dye molecules (Table 1) in the matrix of this crystal. This fact explains the characteristic amplitudes and ranges of manifestation of photoinduced bleaching for the excited subsystems of defects and dye molecules at the increase of the resonance excitation intensity.

The NLO properties of the subsystem of XO molecules in KDP:XO and KDP:XO_{an} crystals in the range $I < I_p$ (Fig. 6a) accompanied with laser radiation self-defocusing, i.e. decrease of on-axis transmittance in the far field (Fig. 6b), shows an essential difference between the real and imaginary parts of the cubic NLO susceptibilities $\chi^{(3)}(\text{KDP:XO}_{an}) \sim 2\chi^{(3)}(\text{KDP:XO})$ (Table 2). In KDP:XO crystal a good overlap of the energy levels of the subsystems of intrinsic defects and dye molecules in the crystal matrix results in concurrence and partial compensation of the response of each of the systems. Due to thermal annealing of defects in KDP:XO_{an} crystal, more efficient NLO response of the subsystem of dye molecules starts to dominate, and this is confirmed by the photoluminescence data.

The comprehensive investigation results of the thermal annealing effect on the spectral and nonlinear optical response of the KDP single crystals doped with Xylenol Orange dye are presented. It was studied the dye molecules and the KDP matrix intrinsic defects contributions into the NLO response due to the self-action of the picosecond laser pulses at second harmonic of mode-locked Nd:YAG laser. The photoinduced refractive index variations have different signs for the intrinsic defects and the organic dye molecules subsystems at the photobleaching range of the crystals. Magnitudes of the real parts of the NLO cubic susceptibilities are significantly different for the KDP:XO and the KDP:XO_{an}: $\text{Re}(\chi^{(3)}) = -6.5 \cdot 10^{-9}$ esu, and $-11.0 \cdot 10^{-9}$ esu correspondingly. The observed competition of the NLO responses can be applied for the parametric frequency conversion phase matching conditions maintaining in the light field of the femtosecond laser sources.

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Вплив термовідпалу на лінійний та нелінійно-оптичний відгук забарвлених KDP кристалів

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Вирощено кристали дигідрофосфату калію, що доповані барвником ксиленоловим помаранчевим (КП), концентрація КП у матриці кристала близько 10 ppm. Виміряно спектральні та люмінесцентні властивості номінально чистого та допованого кристалів, а також допованого кристала, відпаленого при 150°C (KDP, KDP:КП і KDP:КП_{відп.}). Встановлено вплив температури відпалу на ступінь протонування барвника у кристалічній матриці. Аналіз ІЧ-спектра поглинання свідчить про сильну взаємодію молекул барвника з протонною підсистемою матриці. Вивчено нелінійно-оптичні (НЛО) властивості KDP, KDP:КП і KDP:КП_{відп.} кристалів при самовпливі пікосекундних лазерних імпульсів на 532 нм. Припускається, що механізм фотоіндукованого просвітлення та ефекти самофокусування (у KDP) і дефокусування (у KDP:КП і KDP:КП_{відп.}) обумовлені резонансним збудженням підсистеми внутрішніх дефектів та підсистеми молекул барвника відповідно. Показано, що у KDP:КП_{відп.} термовідпал дефектів призводить до домінування більш ефективного НЛО відгука підсистеми молекул барвника, що корелює з даними фотолюмінесценції.