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Growth and characterization of KH_2PO_4 single crystals doped with TiO_2 nanocrystals

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For the first time, the method of temperature lowering was used to grow KDP single crystals from aqueous solutions containing TiO_2 (anatase) nanocrystals. The concentration of TiO_2 in the initial solution varied from 10^{-3} to 10^{-5} M/l. Using the method of three-crystal X-ray diffractometry, the presence of turns of the growth layer packets ~ 3 arcsec was revealed in KDP:TiO_2 crystals for the sectors {100} and {101}. The observed thickness of the growth packets was on the order of 20-30 μm. There was found the sixfold rise of the crystal lattice parameters $\Delta d/d$ in the doped crystal relatively to the pure one caused by incorporation of the nanoparticles into the boundaries of layer-by-layer growth and a formation of semicoherent bond with the crystal. It was found the effect of giant nonlinear optical response of anatase nanoparticles manifestation in KDP crystalline matrix.

Методом снижения температуры впервые выращены кристаллы KDP из водных растворов содержащих нанокристаллы TiO_2 (анатаз). Концентрация TiO_2 варьировалась в исходном растворе от 10^{-3} до 10^{-5} М/л. В кристаллах KDP:TiO_2 методом трехкристальной рентгеновской дифрактометрии установлено наличие разворотов пакетов слоев роста до 3 arcsec для секторов {100} и {101}. Наблюдаемые толщины пакетов слоев роста составляют величину порядка 20-30 мкм. Обнаружено относительное изменение в (6 раз) параметров кристаллической решётки $\Delta d/d$ в легированном кристалле относительно чистого кристалла, которое обусловлено вхождением наночастиц анатаза в границы послойного роста с образованием полукогерентной связи с кристаллом. Показано, что в кристаллической матрице KDP наблюдается эффект гигантского нелинейно-оптического отклика наночастиц анатаза.

Single crystals of potassium dihydrogen phosphate family (KDP, KH_2PO_4) which possess a unique set of physical properties have found wide use in modern optoelectronics and nonlinear optics. Meanwhile, systematic investigation of the relationship between the structure of ferroelectric crystals such as KDP and their nonlinear optical properties from [1, 2] reveals the possibility of the guided impact on the crystals response with tuning their structural properties. As is known [3], the structure of KDP-type fer-

roelectrics is defined by their hydrogen bonds and, consequently, such matrixes readily incorporate both inorganic and organic impurities, e.g. KCl, Oxalic Acid, Al_2O_3, Amaranth, Rhodamine B and Methyl Orange, L-glutamic acid, L-histidine, L-valine [4–7]. The impurities can stabilize single-domain state in ferroelectrics, make phase transition "diffuse", give rise to generation of simulated radiation [8, 9]. A promising trend in the development of up-to-date functional optical materials is incorporation of nanoparticles into the crystalline matrixes of traditional nonlinear optical (NLO) materials for controlled improvement of their nonlinear optical response. For instance, in [10] an attempt was made to design a composite optical material possessing the properties of both active laser and nonlinear optical media, the combination "KDP crystal — SiO_2 particles" being used as a model system. For the first time there was investigated the growth of the crystals from the solutions containing solid micro- and nanoparticles, in static and dynamic (stirring of the solution) regimes. The influence of the size of the particles on the probability of their capture was studied, and the growing crystal was shown to be able to capture effectively $1 \cdot 10^{-2}$–250 μm SiO_2 particles. At the same time, the effect of such inclusions on the functional properties of the crystals was not investigated.

Sometimes it is difficult to investigate the influence of the impurity subsystem on the properties of the matrix by the methods of classic spectral or luminescent analysis, as such methods give only integral characteristics of the crystal properties. A new approach to the said problem is investigation of the NLO response of heterogeneous crystalline systems with self-action of single laser pulses of picosecond range. Due to proper choice of exciting laser radiation wavelength, single- or multi-photon excitation of the subsystem can be realized using such laser beam intensities at which NLO response in the bulk of the matrix does not manifest itself. This method allows to study the effect of crystal structure and crystal defects on photo-induced changes of the refractive index and cross-section of one- or multi-photon absorption of the subsystem [11]. Such a technique has made it possible to reveal the effect of giant NLO response in porous layers of titanium dioxide (TiO_2) nanoparticles at resonance excitation of the surface states - oxygen vacancies. The observed NLO response of the nanosystem is six orders higher than the response of the bulk one [12].

It should be noted that composite materials which contain titanium dioxide nanoparticles evoke deep interest among researches due to the fact that such compounds are promising for the use in optoelectronic devices. In particular, many papers are devoted to the synthesis of high-quality transparent hybrid films of polymer-TiO_2 type. For instance, reported in [13] is the synthesis of polymethylmethacrylate/TiO_2 nanocomposite. In the mentioned paper it is shown that this material which possesses high $\chi^{(3)} \sim 1 \cdot 10^{-9}$ esu cubic NLO susceptibility. The efficient NLO response can find wide application as an effective optical switch. On the base of the combination photopolymer matrix/TiO_2 nanocrystals there have been created bulk holographic diffraction gratings with high diffraction efficiency [14]. The latter essentially rises as the concentration of nanoparticles in the matrix increases, and its value depends on the peak intensity of laser radiation.

In this connection, it seems expedient to consider the system KDP:TiO_2 with TiO_2 nanocrystals (anatase) used as a dopant. Investigation of the systems "nonlinear optical crystal/metal oxide" will allow to find new fields of their application (e.g. NLO media for laser radiation frequency conversion and registration of signals in the visible, IR and THz spectral regions). Moreover, study of such a type of heterogeneous materials may enrich general physical knowledge of the behavior of efficient nonlinear systems.

The goal of the present work was the growth and characterization of a series of KDP crystals with different content of TiO_2 nanocrystals. There was investigated the impact of TiO_2 nanoparticles on the growth kinetics and structure perfection of KDP single crystals. By analyzing KDP:TiO_2 samples photoinduced transmission variation versus the laser excitation intensity there was estimated the contribution of the subsystems of the intrinsic crystal defects and of anatase nanoparicles to the NLO response.

Anatase nanoparticles were obtained by the method of precipitation with subsequent ultra-high frequency (UHF) heating and calcination of the powder, the initial product and the precipitating agent being $TiCl_4$ and ammonia, respectively ($TiCl_4$ was poured into 10 % ammonia solution). The prepared suspension was filtered and washed in distilled water, and the resulting orthotitanic acid H_4TiO_4 was subjected to UHF heating

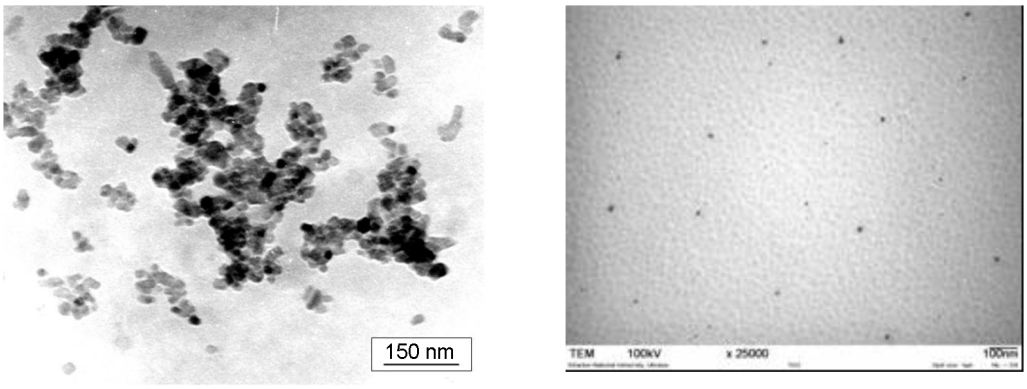

Fig. 1. Electron microscopic image of the synthesized TiO_2 nanocrystals (a) and of those incorporated into the crystal, obtained after dissolution of the grown KDP:TiO_2 crystal in water.

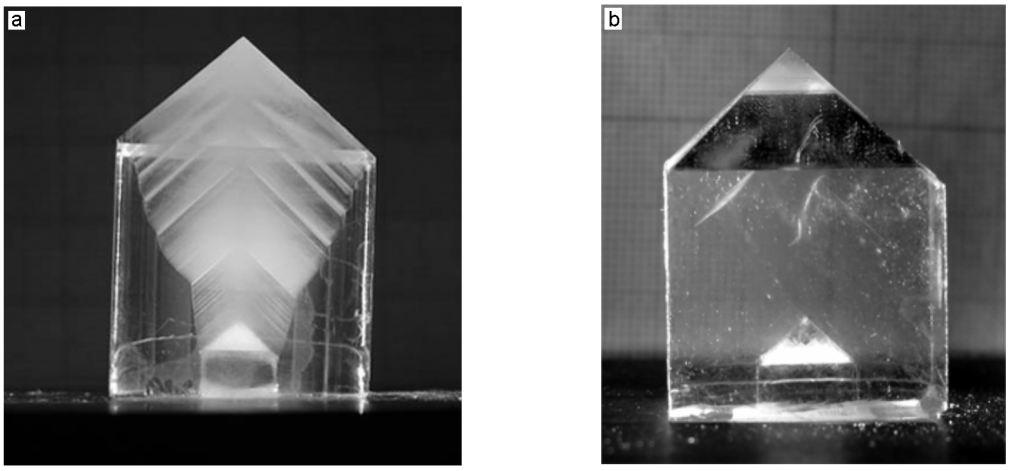

Fig. 2. (a) — as grown anatase doped KDP crystal (TiO_2 concentration in mother liquor solution 10^{-3} wt.%); b — as grown anatase-doped KDP crystal (TiO_2 concentration in mother liquor solution 10^{-4} M/l).

to obtain pyrotitanic acid $H_2Ti_2O_5$. After calcination at 600°C pyratitanium acid transformed into titanium dioxide (TiO_2) with a typical nanocrystal size of 5–15 nm. Electron microscopic picture of the synthesized nanoparticles is shown in Fig. 1a.

KDP crystals doped with TiO_2 nanoparticles were grown in a 5l crystallizer from aqueous solution by the method of temperature lowering [15] on 10×10×10 mm^3 point seeds oriented by the planes (100), (010), (001). The content of controlled microimpurities (Fe, Al, Cr, Mg, Mn and an.) in the initial KH_2PO_4 salt did not exceed 10^{-5} wt%.

The preliminarily prepared suspension containing 40 g of KH_2PO_4 salt, 40 ml of distilled water and TiO_2 nanoparticles taken in a required concentration (10^{-3}, 10^{-4} and 10^{-5} M/l) was dispersed at 65°C. The obtained suspension was placed into the crystal growth apparatus after completion of the process of seed regeneration. To provide dynamical crystal growth regime, the solution contained in the crystallizer was stirred reversively with an interval of 25 s and a pause of 5 s, the rotation velocity being 76 rpm. The value of relative supersaturation was $\sigma^* \sim 2 \div 3$ % at a temperature of solution saturation of 50°C. The initial solution pH changed from 2.0 to 4.0 (±0.1). The growth rate equal to ~ 3 mm/24 hrs provided the obtaining of the crystals with well-developed growth sectors {100} and {101}. The grown crystals are presented in Fig. 2a, b. The concentration of TiO_2 impurity was not observed the effect on the solution pH, the saturation temperature or the crystal morphology. For characterization of the grown crystals there were used satellite samples cut out of the growth sectors {100} and {101} in the form of 10×10×0.8 mm^3 plates with the faces oriented along the crystallographic axes. The working surfaces of the samples had optical polish.

The growth kinetics of pure and anatase doped KDP crystals were investigated in the

process of crystallization from aqueous solution (pH = 4.0±0.1) at natural convection. The time-dependent increment of the crystal size was determined by means of the laser interference-polarization method [16]. A seed of the investigated crystal measuring $10\times5\times1$ mm^3 was placed into a thermostatted dish containing the said solution. At beginning the temperature of the solution and the crystal was several degrees higher than the saturation temperature, and then was smoothly lowered at a rate of 0.75°C per hour. The dependence of the growth rate on supercooling was measured with an error of ~ 2 %. The investigated solutions were preliminarily filtered and overheated at a temperature of 80°C during three days.

The dependences of the growth rate of the faces (101) and (100) on overcooling for pure KDP and for the crystals doped with TiO_2 nanoparticles are shown in Fig. 3. It is seen that in the case of the face (100) such dependences are shifted towards higher supersaturations in comparison with the dependences for the face (101). For the prismatic face the existence of a critical supercooling temperature below which the crystal growth cannot be realized, is connected with adsorption of the impurities of polyvalent metals on the growing face [17]. The obtained data correlate with the experimental results for the pure crystals [18]: at the same supercooling the rate of crystal growth in the direction [001] is higher than that in the direction [100]. As established in the performed experiments, TiO_2 nanoparticles practically do not give effect on the growth of the crystals in both mentioned directions. Unlike e.g. ions of trivalent metals, the nanoparticels contained in the solution do not slow down the growth of the prism faces, and have no essential effect on the growth of the pyramid faces, despite the fact that the particles are captured predominantly by the pyramidal growth sectors.

The impact of 5–15 nm nanocrystalline anatase particles on the matrix structure perfection was investigated by means of three-crystal X-ray diffractometer (TXD) [19]. To realize adequate characterization of the real crystal structure [20], there were chosen the following parameters: the shape of diffraction reflection curve, the rocking curve half-width β, arcsec; the integral power of X-ray reflection I^R and the relative change of the crystal lattice parameters $\Delta d/d$ measured by the method [21].

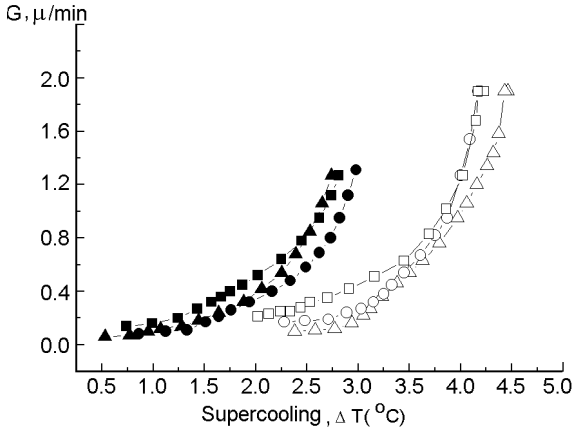

Fig. 3. Dependences of the crystal growth rate (G) on the solution supercooling: •-, ▲-, ■-face (101) for pure KDP, KDP:TiO_2 (10^{-4} M/l), KDP:TiO_2 (10^{-5} M/l); °-, Δ-, □- face (100) for pure KDP, KDP:TiO_2 (10^{-4} M/l), KDP:TiO_2 (10^{-5} M/l).

Preliminary phase analysis of the synthesized TiO_2 nanopowder was performed on the diffractometer of DRON-3M type in $CoK_{\alpha1}$-radiation. The experimental values of the interplanar distances d and the intensities of the diffraction lines completely agree with the tabulated data from the file ASTM No.04-0477 anatase TiO_2 polymorph. The dispersity of anatase powder was determined from the data of X-ray analysis. The average dimension of the coherent scattering regions (D) calculated by the method [22] was ~ 15 nm. The size of TiO_2 particles contained in the crystal measured by electron microscope after dissolution of the grown crystal in water varied from 5 to 15 nm (see Fig. 1b). The area occupied by these particles in the solution was ~ $4.2\cdot10^{-3}$ % and had the density $\rho \sim 4.03\cdot10^{-3}$ cm^{-2}.

X-ray phase analysis (with a determination error of ~ 2 wt. %) did not reveal the presence of anatase nanocrystals in KDP crystals at 10^{-3}–10^{-4} M/l concentrations of TiO_2 in the initial solution on the assumption of the oriented incorporation of all the TiO_2 nanoparticles in the grown crystal. Visually, the obtained crystals had impurity growth bands in the crystallographic direction [100] in the prismatic growth sector, and in the direction [011] in the pyramidal growth sector (Fig. 1a, b). The study of the grown KDP:TiO_2 crystals by TXD method showed the presence of turns of the growth layer packets up to 3 arcsec on the rocking curves (Fig. 4a, b) for the prismatic sectors on the reflexes (080), (008) and for the py-

ramidal sectors on the reflex (066). The thickness of the growth layer packets is about 20–30 μm. For the KDP crystal grown from the same nominally pure raw material and at the same growth parameters the splitting of the rocking curves was not observed. So, in the process of the growth of KDP:TiO_2 crystals the crystallization front rejects the impurity. The nanoparticles are consequently "captured" by the boundaries between the growth layer packets. It gives rise to angular turns of the growth layer packets. Since the thickness of the growth layer packets is 20–30 μm the TiO_2 nanoparticles can be easily "captured" by the growing crystal with subsequent formation of semicoherent bond with with the crystal. It provides two-dimensional distribution order of the TiO_2 nanoparticles at the boundary of the growth layer packets of the crystal. In fact, the measurements of the structure perfection of the doped crystals performed by the method of TXD testify to the presence of such semicoherent boundaries which do not exert an essential effect on the rocking curve FWHM β, the integral reflection power I^R and the crystal lattice parameter in the bulk of the growth layer packet (Table 1). At the same time, more substantial (about sixfold) rise of $\Delta d/d$ is observed for the KDP:TiO_2 samples while measuring the crystal lattice parameters in the growth layer packets (the reflexes (080) and (008), see Table 1). Such changes of $\Delta d/d$ are caused by incorporation of anatase nanoparticles into the boundaries of the layer-by-layer growth followed by the formation of semicoherent bond with the crystal. A similar increase of crystal lattice parameters (Table 1) is also observed for the samples grown from the solution with lower TiO_2 concentration and pH = 2.

It should be emphasized that the observed increase of the crystal lattice parameters in KDP:TiO_2 can change the bonding forces in the crystal lattice of KDP without replacement or withdrawal the cation/anion in the lattice, i.e. without the formation of solid solutions.

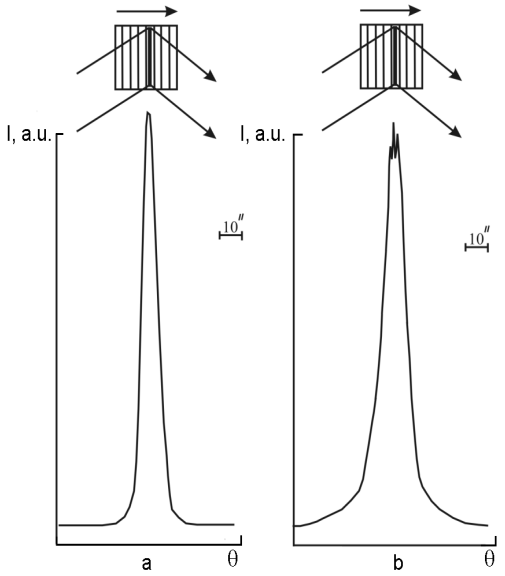

Fig. 4. Shape of rocking curves measured on three-crystal diffractometer in $CuK_{\alpha 1}$ radiation for the reflex (066): (a) — nominally pure KDP crystal; (b) — KDP:TiO_2 crystal.

The linear transmission spectra were measured for pure KDP and KDP:TiO_2 plates with a thickness of ~ 0.8 mm with polished (001) faces (Fig. 5a). The main optical losses in the visible and IR regions were caused by the reflection of light from the input and output faces of the crystal. The pure crystals [23] have different transmission coefficients of the prismatic {100} and pyramidal {101} growth sectors in the UV region of the spectrum. As seen from Fig. 5a (curve *3*), the samples cut out of the pyramidal sector {101} are characterized by higher transmission and by the absence of peculiarities of the spectrum (~ 82 % in the UV- and ~ 90 % in the near IR-region, respectively). For the growth sectors {100} there is observed characteristic decrease of

Table 1. Characterization of structure perfection of nominally pure KDP crystals and KDP crystals doped with nanocrystalline TiO_2 particles

Crystal	Nominally pure KDP, pH = 4			KDP:TiO_2, (concentration of TiO_2 in the initial solution $1\cdot10^{-3}$ M/l, pH = 4)			KDP:TiO_2, (concentration of TiO_2 in the initial solution $1\cdot10^{-4}$ M/l, pH = 2)		
Reflex	β, arcsec	I^R	d, Å	β, arcsec	I^R	$\Delta d/d\cdot10^5$	β, arcsec	I^R	$\Delta d/d\cdot10^5$
(800)	5.2	3.38	0.931354	5.6	3.40	2.1	5.8	3.42	5.0
(080)	6.1	3.41	0.931403	6.2	3.43	12.5	6.3	3.45	14.1
(008)	7.1	7.05	0.871589	7.1	7.12	12.6	7.2	7.20	11.9

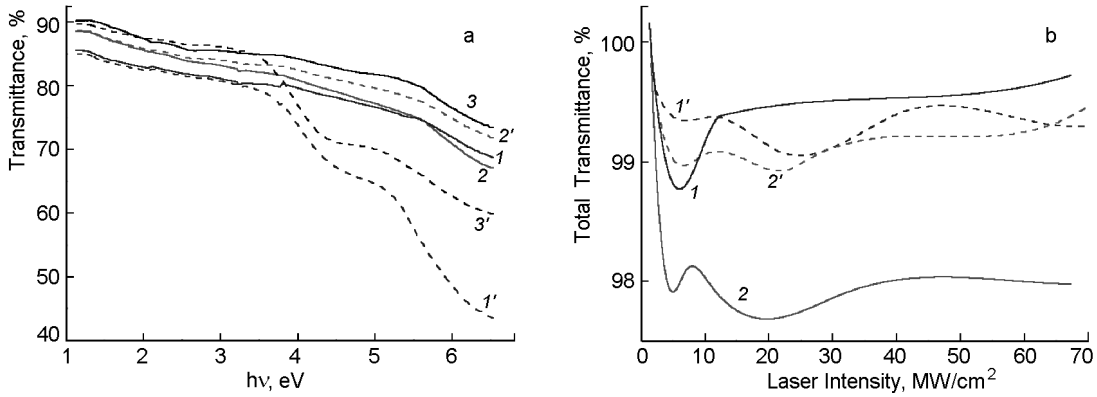

Fig. 5. (a) The linear transmittance (reference air) spectra and (b) the normalized photoinduced total transmittance variation for energy quanta 1.17 eV (1064 nm) vs. peak laser intensity for the KDP:TiO_2 plates with 10^{-5} (*1*) and 10^{-4} (*2*) M/l anatase concentration in mother liquor: reference — NLO response of the pure KDP (*3*). Solid lines correspond to the {101} growth sector, dashed lines with primes — to the {100} sector.

the transmission in the UV-range of the spectrum which makes ~ 70 % at 270 nm wavelength (curve *3'*). The increase of the absorption in the UV-region [15, 23] is defined by the impurities contained in the initial salt, as well as by the coefficients of impurity distribution in different growth sectors. It should be also noted that incorporation of cations of polyvalent metals into KDP crystal lattice leads to the formation of a defect structure of "hydrogen sublattice" caused by proton vacancies. In particular, incorporation of Fe impurity into KDP leads to the appearance of one hydrogen vacancy and two potassium vacancies, the concentration of such defects in the crystal is equal to the total concentration of the cationic impurities [24]. In the visible and IR ranges the growth sectors {100} and {101} transmission spectra (curves *1* and *1'*) are similar to those of the pure KDP for the samples grown from the solutions with 10^{-5} M/l content of TiO_2 nanocrystals. The rise of the concentration of the nanoparticles in the solution up to 10^{-4} M/l increases the transmission of the samples within the whole of the spectrum. Such an effect, especially vivid in the UV-region for the growth sectors {100} (*2'*), should be attributed to the resonance interaction of the intrinsic crystal defects with anatase nanocrystals.

In the case of the crystals grown from the solutions containing ~10^{-3} M/l of TiO_2, many inclusions are formed predominantly in the pyramidal region. This reduces the total transmission within the whole of the spectrum due to effective scattering on optical inhomogeneities.

A detailed study of the nanoparticle system in the matrix of KDP was carried out by analyzing the photoinduced changes of the transmission of the samples at the fundamental wavelength of Nd^{3+}:YAG laser (1064 nm, 1.17 eV quantum energy). The idea of such an approach is the following. The increase of the NLO response of anatase nanocrystals by six orders in comparison with the bulk one due to the resonance excitation of the surface defect states of the nanoparticles makes it possible to register

Table 2. The imaginary part of the cubic NLO susceptibility $Im(\chi^{(3)})$ and photodarkening saturation intensity I_s for the pure KDP (reference air) and KDP:TiO_2 (reference pure KDP) with different concentration of TiO_2 nanoparticles in the initial solution

Sample	Concentration TiO_2, M/l	Reference	{100} sector		{101} sector	
			$Im(\chi^{(3)})$, 10^{-9} esu	I_s, MW/cm^2	$Im(\chi^{(3)})$, 10^{-9} esu	I_s, MW/cm^2
KDP	–	air	0.9	7.9	0.3	8.4
KDP:TiO_2	10^{-5}	KDP	0.3	7.0	1.3	6.0
KDP:TiO_2	10^{-4}	KDP	1.2	6.6	2.7	5.0

the photo-induced changes of the optical parameters of the whole of the heterogeneous system, even at low nanoparticle concentration in the matrix due to the giant NLO response of anatase nanoparticles [12].

The scheme of the experimental investigation of the NLO response is described in [12]. Single picosecond laser pulses (42 ps FWHM, repetition rate 5 Hz) with the Gaussian spatial profile were focused on the sample by a lens with a focal distance of 11 cm (the distance between the lens and the sample was 20 cm and remained unchanged). The incident radiation intensity was changed using a neutral attenuator with 1 – 50 % transmission variation. The used technique allowed to study the NLO response from the same aperture of the incident beam for laser radiation intensities ranging between 1 and 100 MW/cm^2 at high signal-to-noise ratio. From the dependences of the total transmission of the samples on the incident radiation intensity I there was determined the imaginary part of the cubic NLO susceptibility $Im(\chi^{(3)})$ characterizing the photo-induced changes of the optical absorption $\Delta\alpha_{NLO} \sim Im(\chi^{(3)})I$.

The total transmittance dependencies versus the peak laser intensity for the pure KDP samples are nonmonotonic. At laser radiation intensities up to 8 MW/cm^2 there is observed the effect of two-photon absorption which leads to the photo-induced reduction of the transmission by 2 % (the sector {101}) and 3 % (the sector {100). Such an effect is due to the resonance two-photon excitation of the intrinsic defects [25] of the pure KDP crystal. It is characterized by rather high values of the imaginary part of the cubic NLO susceptibility $Im(\chi^{(3)}) \sim 3.4 \cdot 10^{-10}$ and $9.4 \cdot 10^{-10}$ esu, respectively (see Table 2), and is accompanied with the effect of laser beam self-defocusing. Further rise of the intensity is characterized by the NLO dependences earlier observed at single-photon resonance excitation of the defect states of KDP crystals at 532 nm wavelength. The photoinduced darkening is replaced by the bleaching of the samples by 1 % and self-focusing of the laser beam transmitted through the sample. Both of these processes are saturated at a peak intensity of ~17 MW/cm^2 which is by an order higher than the typical saturation intensities at single-photon excitation.

To extract the NLO contribution of the subsystem of anatase nanoparticles from the response of the doped samples, the dependences of the photoinduced variation of the total transmission of the doped crystals were normalized to the analogous dependences for pure KDP taking into account the sectorial structure of the crystal. Shown in Fig. 5b are the dependences of the total transmission of the doped samples on the incident radiation intensity at 1064 nm wavelength. Despite the fact that the spectral characteristics of the doped crystals have no particularly pronounced peculiarities in the transparency region, all the samples show considerable NLO response. This is caused by the action of two mechanisms: the resonance excitation of the intrinsic defect structure of the pure crystals and of the surface states of TiO_2 nanoparticles [12].

All the doped samples are characterized by the photo-induced decrease of the transmission at low excitation intensities (Fig. 5b). Table 2 contains the values of the saturation intensity I_s at which the photo-induced darkening is replaced by the bleaching of the subsystem. The presented dependences are reversible, i.e. recurring both at the rise and the decrease of the incident radiation intensity. Thus, due to the use of picosecond pulses the effects of accumulation were not observed in the investigated crystals. For $I < I_s$ there were calculated the values of the imaginary part of the cubic dielectric susceptibility $Im(\chi^{(3)})$. The simulation results are presented in Table 2.

The dependences shown in Fig. 5b testify to an essential distinction in the NLO changes of the total transmission of the doped samples cut out of different crystal growth sectors. Due to the resonance effect of two-photon absorption on the intrinsic crystal defects, the photo-induced changes of the total transmission effectively characterize the KDP structure perfection. In particular, the prismatic sectors of pure KDP crystals are characterized by higher concentrations of the defects and, consequently, by higher values of the imaginary part of the cubic NLO susceptibility $Im(\chi^{(3)})$ (see Table 2) in comparison with the corresponding values for the pyramidal sectors.

Doping of KDP with TiO_2 nanocrystals proves the assumption formulated while analyzing the transmission spectra: incorporation of anatase nanoparticles diminishes the contribution of the optical and NLO response of the subsystem of the intrinsic defects. For the pyramidal growth sector the contribution of the NLO response of the system of nanocrystals predominates, and the saturation intensity I_s of the photo-induced darkening essentially decreases. At 10^{-4} M/l concen-

tration an effeciency of the NLO response of the nanoparticles practically by an order exceeds the contribution of the resonance two-photon absorption on the intrinsic crystal defects. For the prismatic growth sector the presence of high concentration of the intrinsic defects makes the contributions of the both of the systems to the NLO response comparable. Thereat, it should be noted that the measured imaginary parts of the cubic NLO susceptibility of the subsystem of anatase nanoparticles in the sector {100} are by several times smaller than the corresponding values for the sector {101}.

Thus, for the first time we have grown KDP single crystals doped with anatase nanocrystals with the characteristic particle size 5–15 nm. It is shown that all the crystals grown in the presence of the nanoparticles with 10^{-3}–10^{-5} M/l concentrations are characterized by impurity streakiness both in the growth sectors {101} and {101}. Most vividly impurity streakiness manifests itself in the sectors {101} at 10^{-3} M/l concentration of TiO_2. It is established that the concentration of the nanoparticles in the solution on the order of 10^{-3}–10^{-5} M/l does not influence the growth rate of the doped crystals when the growth is realized under the conditions of natural convection. The X-ray data analysis shows that in the process of the growth of TiO_2-doped KDP crystals the nanoparticles are rejected by the crystallization front and then "captured" by the boundaries between the growth layer packets. This seems to lead to angular turns of the growth layer packets with subsequent formation of semicoherent bond with the crystal. It provides two-dimensional distribution order of the TiO_2 particles at the boundary of the growth layer packets of the crystal. The revealed rise of the crystal lattice parameters in the crystals doped with anatase nanocrystals reflect the changes in the bonding force in the crystal lattice of KDP:TiO_2. It was found that the effect of the giant nonlinear optical response of anatase nanoparticles takes place in the crystal matrix of KDP, and its manifestation essentially depends on the crystal structure of the matrix.

It was shown that application of the competitive resonant NLO response contributions of the intrinscic KDP defects and anatase nanoparticles sybsystems is a promising approach for the efficient functional KDP:TiO_2 material with controllable NLO response design.

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Вирощування та властивості монокристалів KH_2PO_4, що доповані нанокристалами TiO_2

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Методом зниження температури вперше вирощено кристали KDP з водних розчинів, що містять нанокристали TiO_2 (анатазу). Концентрація TiO_2 варіювалася у початковому розчині від 10^{-3} до 10^{-5} М/л. У кристалах KDP:TiO_2 методом трьохкристальної рентгенівської дифрактометрії встановлено наявність розворотів пакетів шарів росту до 3 arcsec для секторів {100} та {101}. Товщина пакетів шарів росту, що спостерігається, складає величину 20-30 мкм. Виявлено відносну зміну (у 6 разів) параметрів кристалічної решітки $\Delta d/d$ у легованому кристалі щодо чистого кристала, яка обумовлене входженням наночастинок анатазу у межі пошарового росту з утворенням напівкогерентного зв'язку з кристалом. Показано, що у кристалічній матриці KDP спостерігається ефект гігантського нелінійно-оптичного відгуку наночастинок анатазу.