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Self-focusing effect on the second harmonic generation in the KDP single crystals with incorporated anatase nanoparticles

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Second harmonic generation efficiency versus the TiO_2 nanoparticles concentration incorporated in the KDP single crystals was studied within picosecond range pump pulses at 1064 nm. For the first time we have obtained the frequency conversion efficiency enhancement in the KDP:TiO_2 in comparison with the KDP crystals due to the internal self-focusing effect that was observed as the pump beam spatial profile narrowing at moderate peak intensities.

Исследована зависимость эффективности генерации второй гармоники от концентрации наночастиц TiO_2, инкорпорированных в монокристаллическую матрицу KDP, при возбуждении пикосекундными лазерными импульсами на длине волны 1064 нм. Впервые показано усиление эффективности преобразования частоты излучения в монокристаллах KDP:TiO_2 по сравнению с KDP благодаря эффекту внутренней самофокусировки, который проявляется в сужении пространственного профиля пучка накачки при умеренных интенсивностях возбуждения.

1. Introduction

Single crystals (SCs) of potassium dihydrogen phosphate (KDP, KH_2PO_4) have a great variety of applications in nonlinear optics, photonics and optoelectronics fields. They belong to those few materials widely used in industrial laser facilities as frequency multipliers, parametric amplifiers and electrooptical shutters. The unique combination of properties like wide range of transparency, relatively high magnitudes of the quadric nonlinear susceptibility, electrooptical and piezooptical effects, as well as the possibility of growing wide aperture crystals, KDP SCs draw special attention of the researches. It is also an ideal model system to study the effect of intrinsic and extrinsic defects in complex oxide insulators.

Improving nonlinear optical (NLO) properties of the KDP crystals, the optical harmonic generation efficiency in particular, it is possible to increase significantly the range of energies/intensities of laser radiation. Use of the modern nanotechnology for manufacturing of new composite materials leads to creation of nanocomposite structures with unique optical and NLO properties.

In several papers [1, 2] the KDP matrix has been successfully used as a host of nanoparticles (NPs). NPs are having an increasing importance due to their effect on the mechanical, electric, optical and magnetic properties. It was shown that anatase modification of titanium dioxide NPs form a periodic structure in the KDP SC [2]. The presence of nanocrystals in the KDP SCs does not reduce its optical quality [3] but significantly affects its cubic NLO response [2]. The paper presents an attempt to control the quadric response of the KDP:TiO_2 SCs within the cubic refractive NLO response of the guest-host media.

2. Materials and methods

Nominally pure KDP SCs and crystals with incorporated TiO_2 NPs (anatase modification) were grown by the temperature reduction method [1] onto a 10×10×10 mm^3 point seed. The anatase NPs were obtained by the method of precipitation with subsequent microwave heating and calcination of the resultant powder. The average dimension of anatase NPs determined from the data of transmission electron microscopy and X-ray analysis was about 15 nm. The concentration of the NPs in the growth solution varied from 10^{-5} to 10^{-3} wt. %. Incorporation of TiO_2 NPs in the crystal matrix does not reduce significantly the growth rate.

The structure perfection study in Bragg and Laue geometries of the grown KDP:TiO_2 crystal showed the presence of angular turns up to 3 arcsec on the rocking curves for the growth layer stacks [2]. In the growth process of KDP:TiO_2 crystals the nanoparticles are pushed aside from the crystallization front, and then "captured" by the boundaries between the growth layer stacks, which causes the angular turns, not observed in nominally pure SCs. This indicates the appearance of semicoherent boundary between the growth layer stacks and the formation of two-dimensional ordering of TiO_2 nanoparticles in the bulk of the crystal. Besides, scanning electron microscopy study of the surface relief of KDP:TiO_2 SC showed the presence of quasi-equidistant layers with average spatial period of 15 μm. The anatase NPs incorporation does not reduce significantly the laser damage threshold of KDP:TiO_2 SCs with concentration up to 10^{-4} wt. % of TiO_2 [4].

There were two sets of the SC samples studied: "thin" (10×10×0.8 mm^3) and "thick" (10×10×10 mm^3) plates, cut along the II type of phase matching direction (*oe–e* interaction) for the second harmonic generation (SHG) at 1064 nm, the fundamental wavelength of Nd:YAG laser. All boundaries of the samples were finished with optical polishing, with faces oriented along phase-matching direction and polarization of *o*- and *e*-waves.

Table. Characterization data of KDP and KDP:TiO_2 SCs: TiO_2 concentration in growth solution, NPs concentration in SC, absorption coefficients α_ω and $\alpha_{2\omega}$ at 1064 nm and 532 nm wavelengths correspondingly, the slope magnitude p of $\mathcal{E}_{2\omega}$ versus $\mathcal{E}_\omega$ dependency in log-log scale that characterizes the order of the NLO response, the quadric NLO coefficient d_{36}

	KDP	KDP:TiO_2	
SCs notation	Pr	Pr5	Pr4
TiO_2, wt.%	–	10^{-5}	10^{-4}
NPs conc., cm^{-3}	–	$1.6\cdot10^{10}$	$1.6\cdot10^{11}$
α_ω, m^{-1}	4.5	5.3	6.8
$\alpha_{2\omega}$, m^{-1}	6.3	7.2	8.4
p	2.0	2.0	2.1
d_{36}, pm/V	0.40	0.38	0.35

A scheme of experimental setup used for the SHG efficiency and the quadric nonlinear coefficient d_{36} measurement with phase-matched method [5] is presented in Fig. 1. The beam with Gaussian spatial profile of mode-locked Nd:YAG laser (pulsewidth 42 ps (FWHM) at 1064 nm, 5 Hz repetition rate) passed through focusing lens L (f = 11 cm). The SCs were positioned at 2 cm after the waist, with faces adjusted diagonally to the polarization of the pump beam in order to provide the equal energy splitting between *o*- and *e*-waves. The photodiodes PD1 and PD2 were used to measure the input/transmitted ($\mathcal{E}_\omega / \mathcal{E}_\omega^T$) pulse energies, and PD3 — the SH ($\mathcal{E}_{2\omega}$) one. The transmitted fundamental and SH pulses were distributed with interference dichroic mirror (DM) and appropriate bandpass filters BF1/BF2. The simultaneous measurement of transmitted fundamental and SH energies makes it possible to distinguish the contributions of frequency conversion and non-radiative losses in extinction of the incident beam. All registration channels were absolutely calibrated with power/energy meter VEP-1L.

The KDP and KDP:TiO_2 crystals cut from prismatic grows sector were used for investigation. The samples notation, TiO_2 and NPs concentrations, as well as linear absorption coefficients at fundamental (α_ω)

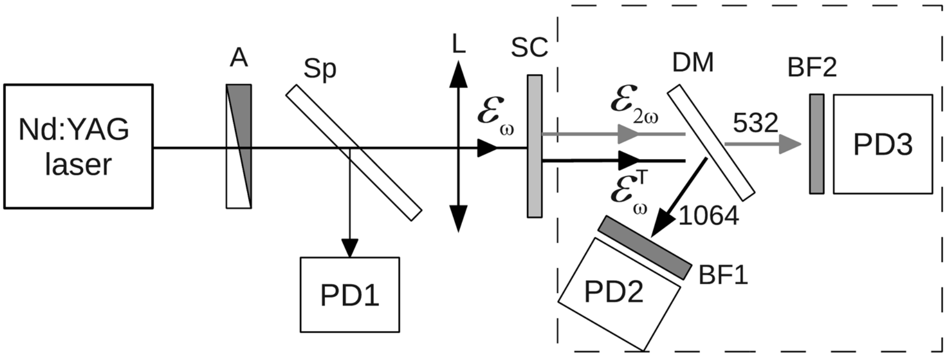

Fig. 1. The experimental setup scheme: A — neutral attenuator; Sp — beam splitter; L — focusing lens; SC — single crystal; DM — dichroic mirror; PD1, PD2 and PD3 — photodiodes; BF1 and BF2 — bandpass filters; $\mathcal{E}_\omega$, $\mathcal{E}_\omega^T$ and $\mathcal{E}_{2\omega}$ — the energies of incident, transmitted and SH pulses, respectively.

and SH ($\alpha_{2\omega}$) wavelengths data are presented in Table.

The energy conversion efficiency $\eta = \mathcal{E}_{2\omega}/\mathcal{E}_\omega$ into the SH in the given pump field approximation was obtained from the power conversion efficiency [5] with account of the reflection losses at the SC/air interfaces and temporal averaging across the incident Gaussian pulse profile:

$$\eta = \frac{8\sqrt{2\pi}L^2|d_{eff}|^2\exp[-L(\alpha_\omega + \alpha_{2\omega}/2)]\mathcal{E}_\omega}{c\tau\varepsilon_0[\lambda_{2\omega}a(1 + n_\omega^0)(1 + n_\omega^e)(1 + n_{2\omega}^e)]^2},$$

where $n^{o,e}_{\omega,2\omega}$ – refractive indices of the ordinary and extraordinary beams at proper wavelengths, $d_{eff} = d_{36}\sin(2\theta)$ – the effective quadric NLO coefficient, $\theta = 59°$ – angle between the optical axis and II type phase matching direction in the KDP [6], c – the speed of light, ε_0 – the dielectric constant, τ and a are the incident pulsewidth and beam radius (HW1/eM), L – SC thickness.

For the SHG process $\mathcal{E}_{2\omega} \sim \mathcal{E}_\omega^p$ with $p = 2$ without account of other NLO process manifestation. The slope p reflects the order of the optical nonlinearity for the $\mathcal{E}_{2\omega}(\mathcal{E}_\omega)$ dependency in the log-log scale. Meanwhile the SH conversion efficiency is $\eta \sim \mathcal{E}_\omega$ with a coefficient that contains $|d_{36}|$.

In order to study the impact of cubic refractive nonlinearity on SH generation process of KDP:TiO_2 SCs, the analysis of beam spatial profile transformation after the sample @1064 nm was performed. With this purpose, the SHG registration system (showed as dashed rectangle in Fig. 1) was replaced by CCD-based beam profiler Ophir Spiricon SP-620U (1600×1200 px, 4.4 μm pixel spacing). The spatial profile of freely propagating and transformed beam was registered in 6 cm after the output face of the sample. We adjusted the polarization of the incident beam along one of the sample faces (polarization of *o*- or *e*-waves) in order to suppress *oe–e* parametric interaction.

The high-frequency noise of the spatial profile was removed by Fourier low-pass filter. Then, averaging over concentric shells with 5 px width, centered on a beam energy center, was held in order to obtain averaged radial distribution. This made it possible to analyze the profile trasformation after the sample depending on the intensity of incident radiation.

3. Results and discussion

The experimental data on the SHG in the KDP and KDP:TiO_2 SCs cut from the prismatic growth sector are shown in Fig. 2. The SH pulse energy $\mathcal{E}_{2\omega}$ versus the fundamental one $\mathcal{E}_\omega$ is presented in double logarithmic scale for the "thin" (a) and "thick" (b) SC sets with different concentrations of anantase NPs. All the dependencies have an average slope (nonlinearity order) $p = 2.0\pm0.15$ up to $\mathcal{E}_\omega \sim 40$ μJ (peak pump intensity 2 GW/cm^2). Estimated p for the "thin" SCs set are presented in Table 1. We should point out a reduction of the effective NLO response order $p = 1.8\pm0.1$ for the KDP:TiO_2 at $\mathcal{E}_\omega > 50$ μJ for both sets. For the "thick" KDP:TiO_2 SC we have observed the rise of the effective NLO response order $p = 2.3\pm0.05$ at the initial range ($\mathcal{E}_\omega < 15$ μJ).

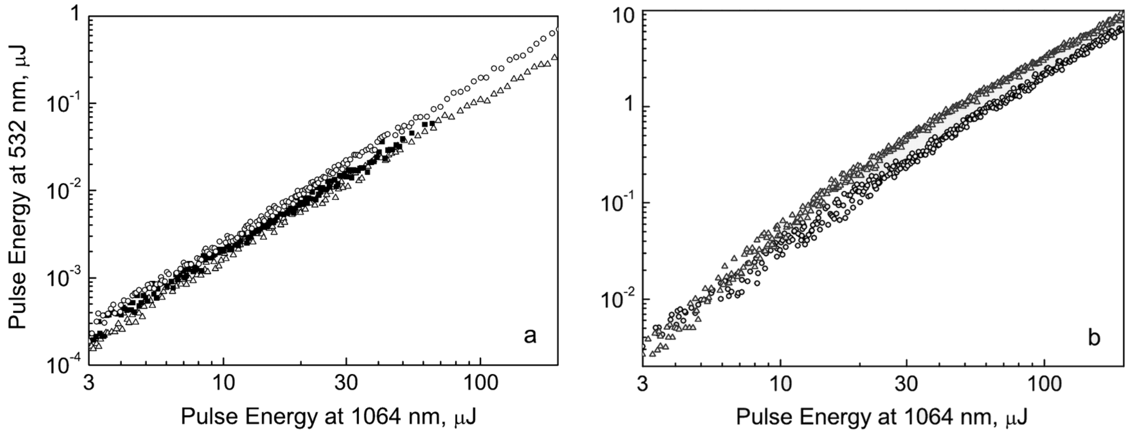

Fig. 2. The second harmonic pulse energy versus the fundamental one for the "thin" (a, 0.8 mm) and the "thick" (b, 10 mm) KDP (O, Pr) and 10^{-5} (■, Pr5) and 10^{-4} (Δ, Pr4) TiO_2 wt.% KDP:TiO_2 single crystals.

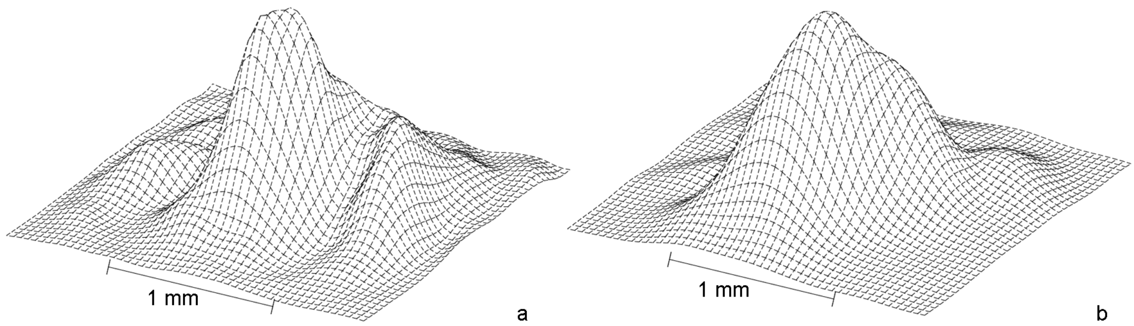

Fig. 3. The comparison of laser beam profiles transformation after the sample @1064 nm: (a, Pr4) — KDP:TiO_2, 10^{-4} wt. %; (b, Pr) — KDP.

The obtained data give possibility to derive $\eta(\mathcal{E}_\omega)$ dependencies and to estimate the magnitudes of the quadric NLO coefficients $|d_{36}|$ in the given pump field approximation without impact of the higher order NLO effects. The $|d_{36}|$ values for the "thin" KDP and KDP:TiO_2 SCs are presented in Table. The estimations were performed for $\mathcal{E}_\omega < 40$ μJ pump pulse energy range. For the nominally pure KDP we have obtained $d_{36} = 0.40\pm0.01$ pm/V that corresponds to the reference data [6, 7]. The NPs incorporation causes the effective d_{36} magnitude reduction up to 10 % for the KDP:TiO_2 (Pr4).

The hydrogen bonds in KDP crystals have small contribution to SHG efficiency, while $[PO_4]^{3-}$ tetrahedral units contribute about 99 % to SHG coefficients [8]. In comparison with them, the volume fraction of anatase nanoparticles in KDP:TiO_2 SCs is low. Therefore we suggest that there is no significant change of the quadric nonlinear coefficient and it does not depend on anatase NPs concentration. And the observed decreasing of SHG efficiency in the "thin" KDP:TiO_2 SCs is caused by manifestation of photoinduced absorption processes in KDP with embedded TiO_2 NPs. In nominally pure KDP SCs we have observed the photoinduced bleaching effect at the wavelength of SHG (532 nm) [9], while TiO_2 nanocrystals lead to the enhancement of photoinduced absorption. These processes rapidly saturate with the SH energy growth at 532 nm. As a result, they significantly contribute to SHG efficiency in the "thin" single crystals, whereas in the "thick" one the opposite situation is observed.

We have obtained an enhancement of the SHG process efficiency in "thick" KDP:TiO_2 crystal relatively to the KDP one (Fig. 2b). We propose that the possible mechanism of the efficiency rise in KDP:TiO_2 is the interaction between the quadric NLO response of the matrix and the cubic one of anatase NPs. The study of the spatial profile distortion in SCs with/without TiO_2 NPs at different intensities of incident pump radiation proofs this suggestion.

The 3D images of transmitted laser beam profiles captured with CCD beam analyzer

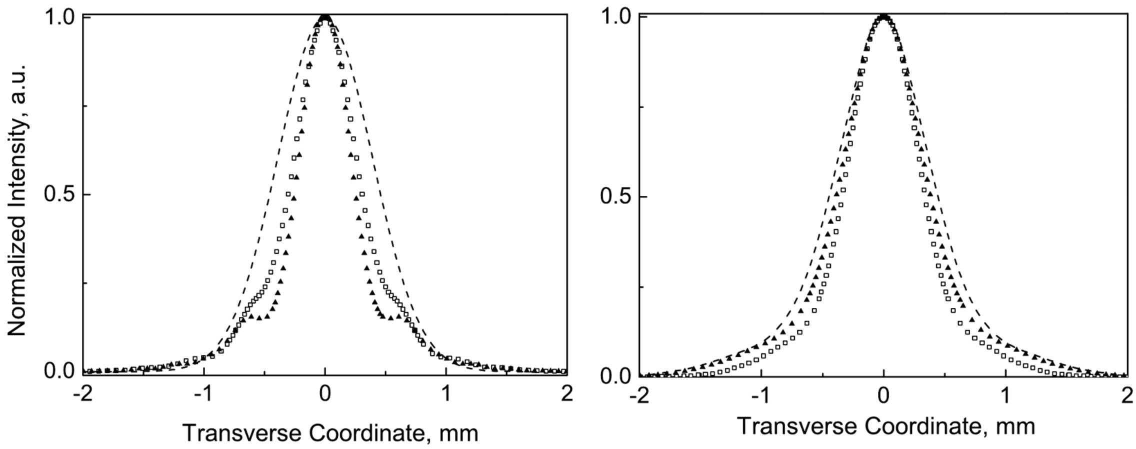

Fig. 4. Spatial laser beam profiles transformation (at 1064 nm) after KDP:TiO_2 (a, Pr4) and KDP (b, Pr) single crystals at the peak pump intensities 40 MW/cm^2 (▲) and 4.4 GW/cm^2 (□). Dashed line — freely propagating laser beam. All the data are normalized on unity.

behind the "thick" SCs are presented in Fig. 3 at moderate peak pump intensity 40 MW/cm^2. In KDP:TiO_2 (Pr4) SC (a), the effective transformation of the beam is observed, while almost negligible distortion of the beam profile takes place in Pr one (b).

The beam kern and aberration pattern formation is determined by the developed internal self-focusing of the pump beam in the KDP:TiO_2. For the "thin" samples a slight distortion of transmitted laser beam was observed earlier [2], and registered in the far field after the sample (so-called, external self-focusing). The distinction between KDP and KDP:TiO_2 SCs behavior is explained by the giant cubic nonlinear response of anatase NPs [10].

Applying the described spatial averaging procedure we have obtained the transverse spatial profiles that are presented in Fig. 4: cross-sections at 6 cm behind (a) KDP:TiO_2 (Pr4) and (b) KDP(Pr) SCs. Dashed lines corresponds to the freely propagating laser beam without crystals. Profiles are presented at moderate (40 MW/cm^2, ▲) and high (4.4 GW/cm^2, □) incident intensities. At the moderate intensity Pr4 SC (a) demonstrates effective narrowing of the beam kern and the appearance of the plateau that corresponds to the averaged aberration pattern (see Fig. 3a), while for Pr SC we have observed slight beam compression (b). One hundred times the peak pump intensity rise (□, 4.4 GW/cm^2) causes the saturation of anatase NPs NLO response. We have observed similar narrowing of the beam in both Pr and Pr4 SCs, which is determined by self-focusing effect of the matrix at GW/cm^2 peak pump intensity range [11].

As a result we can conclude that at the moderate pump intensity range the efficient internal self-focusing in KDP:TiO_2 SC caused by the giant anatase NPs NLO response provides the effective pump energy concentration and enhancement of the frequency conversion efficiency in comparison with the nominally pure KDP single crystal.

4. Conclusions

Thus, nominally pure KDP and doped KDP:TiO_2 crystals were grown from aqueous solution by the temperature lowering technique. Second harmonic generation efficiency versus the incorporated TiO_2 nanoparticles concentration was studied within picosecond range pump pulses at 1064 nm for the "thin" (0.8 mm) and "thick" (10 mm) SCs sets. About 10 % of quadric NLO coefficients d_{36} magnitude reduction was observed for the "thin" KDP:TiO_2 SCs. We suggest that the photoinduced absorption by anatase NPs at SH wavelength can give the main contribution into the observed reduction effect.

For the first time we have obtained the frequency conversion efficiency enhancement in the "thick" (10 mm) KDP:TiO_2 in comparison with KDP crystals due to the internal self-focusing effect that was observed as the pump beam spatial profile narrowing at moderate peak intensities up to 100 MW/cm^2. Thus for the composite system (water-soluble matrix with metal oxide nanoparticles) the possibility of quadric nonlinear optical response control with the cubic one is shown.

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Вплив самофокусування на ефективність генерації другої гармоніки у монокристалах KDP з інкорпорованими наночастинками анатазу

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Досліджено залежність ефективності генерації другої гармоніки від концентрації наночастинок TiO_2, інкорпорованих у монокристалічну матрицю KDP, при збудженні пікосекундними лазерними імпульсами на довжині хвилі 1064 нм. Вперше показано підсилення ефективності перетворення частоти випромінювання у монокристалах KDP:TiO_2 у порівнянні з KDP завдяки ефекту внутрішнього самофокусування, що проявляється у звуженні просторового профілю пучка накачки при помірних інтенсивностях збудження.