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Effect of incorporation of titanium dioxide nanocrystals on bulk properties of KDP crystals

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ABSTRACT

The impact of titanium dioxide (anatase) nanocrystals on growth process, optical and structural properties of KDP single crystal was studied. As-grown crystals were characterized by High Resolution Three-crystal X-ray Diffractometer, optical diagnostics of elastic scattering, cone-shaped interference method, and spatial profile analysis method. In the composite system KDP:TiO_2 the effect of giant nonlinear optical response of anatase nanoparticles was revealed, in particular in the intensity range up to 20 MW/cm^2 the change of sign of the nonlinear refraction index was found. These results can be explained by the resonance excitation of defective states on TiO_2 nanoparticle surface.

1. Introduction

Single crystals of Potassium Dihydrogen Phosphate (KDP, KH_2PO_4) attract much attention due to their wide applications in different fields of nonlinear optics, optoelectronics and photonics [1–3]. Moreover, such crystals are interesting as model objects [4,5] for studying the mechanism of crystal growth in the presence of different impurities, as well as for finding out the relation between the crystal structure and nonlinear properties. These crystals possess a unique set of optical properties: a wide transparency range, electrooptical and piezooptical effects, relatively high values of second-order nonlinear susceptibility. Advanced growth methods make it possible to obtain sufficiently perfect KDP crystals with an aperture of $\sim 50 \times 50$ cm^2 [6–9].

During the past years, an impetus has been given to the development of the methods of effective conversion of laser radiation owing to the use of new ranges of coherent radiation frequencies and the improvement of radiation detection methods. In this connection, there should be mentioned extension of the spectral range of narrow-band continuously frequency-tuned laser radiation from UV to IR ranges, development of the methods of radiation frequency conversion [10], detection of THz radiations [11], improvement of the methods for radiation wave front correction [12]. The use of condensed media in diagnostics of fast processes, nonlinear laser spectroscopy and other branches of applied physics has stimulated search for new nonlinear media possessing the set of optical properties required for particular task, as well as modification of the existing nonlinear optical (NLO) media.

Numerous studies have been performed to find out possible methods for raising the efficiency of laser radiation conversion by modifying the structure of the well-known nonlinear optical single crystals (KDP, ADP, $LiNbO_3$) [13–19] or creating composite semi-organic or organic–inorganic nonlinear optical media [20,21]. Search for new NLO media to be used in optoelectronics and nonlinear optics has stimulated creation of nanocomposite materials, which can be obtained by proper incorporation of metal oxide nanoparticles (MONPs) into dielectric matrixes. Owing to their ultra-fast nonlinear optical response and giant Kerr effect, such materials can be used as nonlinear optical switches and nonlinear optical limiters for conversion of laser radiation in pico- and femtosecond range. Collective excitation of free carriers in the nanoparticles by electromagnetic light wave with subsequent essential local field enhancement give rise to different resonance optical effects which occur in the nanoparticles in a wide spectral range. From the viewpoint of realization of nonlinear optical properties, MONPs with enhanced concentration of free carriers have indisputable advantage. It should be noted that in anatase (TiO_2) nanocrystals which possess super-high ability to accumulate excitations under the action of pico- and femtosecond pulses and to generate free carriers in nanosecond range, giant nonlinear optical

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response serves as a “concentrator” inside the electrooptical matrix which amplifies photoinduced (quadratic) polarization in THz (optical rectification) and visible (SHG) spectral ranges.

Nowadays, special attention is being paid to the development of new hybrid inorganic/organic liquid crystal materials, since dispersion of different nanoparticles in liquid crystals leads to the design and development of new liquid crystal devices (LCDs) with electro-optical effects [22,23] or photorefractive effects [24] enhanced by the incorporation of semiconductive nanoparticles. As shown [25], the nanocomposite polymehtylmethacrylate/TiO_2 has high cubic nonlinear optical susceptibility ($\sim 10^{-9}$ esu) and ultra-fast response time. So, it can be used as an effective nonlinear optical switch. The technology of laser imprinting [26] was developed for 3D structures based on TiO_2 into a polymer matrix. By changing the size of the nanoparticles and the type of their consolidation (isolated particles, linear and 3D structures) one can modify the material for different applications in photonics.

Due to its crystallographic characteristics KDP single crystal possesses a strong capability to incorporate guest species such as ammonium or substituted ammonium groups [27–29]. Recently we have shown the possibility to grow KDP single crystals containing incorporated anatase nanocrystals [30]. The KDP single crystalline matrix was chosen for the TiO_2 incorporation under the assumption of:

(1) the possibility to input the anatase nanoparticles into mother liquor at the stage of the crystal matrix growth;
(2) the possibility of strong coupling of protons, potassium and $H_2PO_4^{3-}$ ions with active sites (in particular, with oxygen vacancies) on the surface of the nanoparticles both in the growth solution and in the crystal matrix;
(3) the possibility to control the hydrogen bonds system in the crystalline matrix by means of photoinduced giant local fields at the TiO_2 nanocrystal surface with resonance excitation of their surface defect states due to the “soft” hydrogen bonding structure of the KDP crystal;
(4) the possibility of the creation and annihilation of pair defects in the KDP crystal due to reduction–oxidation processes at the nanoparticles surface, i.e. the generation of hydrogen vacancy and the creation of interstitial hydrogen atom (typical intrinsic defects).

It has been found that the effect of giant nonlinear optical response of anatase nanoparticles in KDP crystal matrix substantially depends on the character of incorporation and distribution of these nanoparticles in the matrix and on the structure perfection of the matrix itself [30].

The present paper gives new data on the growth kinetics, structure perfection and nonlinear optical properties (photoinduced refraction and absorption) for KDP crystals with incorporated TiO_2 nanoparticles which will make it possible to establish the relation between the real structure and nonlinear optical properties of the composite KDP:MONPs.

2. Experimental section

2.1. Crystal growth

Nominally pure KDP single crystals and the ones with incorporated TiO_2 nanoparticles were grown by the temperature reduction method [6] onto $10 \times 10 \times 10\ mm^3$ point seed. The initial KH_2PO_4 salt was synthesized from the high purity reagents H_3PO_4 and KOH, the content of the impurities (Fe, Al, Cr, Mg, Mn, etc.) in the salt did not exceed 10^{-5} wt.%. The solutions were filtered through filters with a pore diameter of 0.05 μm. Prior to the experiment, the solutions were overheated at 80 °C. The anatase nanoparticles were obtained by the method of precipitation with subsequent microwave heating and calcination of the resultant powder [30]. The dimension of the anatase nanoparticles determined from the data of transmission electron microscopy and X-ray analysis was 15 nm [30].

The suspension prepared preliminarily and containing KH_2PO_4 salt (40 g), twice distilled water (100 ml) and TiO_2 nanoparticles in the required concentration (10^{-3}, 10^{-4} and 10^{-5} wt.% in terms of the 2000 g KH_2PO_4 salt), was dispersed at T = 65 °C. The obtained suspension was added into a 5L crystallizer after termination of the process of seed regeneration. To provide dynamic crystal growth conditions, the solution in the crystallizer was stirred at a velocity of 76 rpm. The relative supersaturation σ^* amounted to $\sim$2–3% at a temperature of solution saturation of 50 °C; $\sigma^* = (C - C_o)/C_o$. The pH values of the mother liquor were 2.0 and 4.0 (±0.1). The average crystal growth rate was $\sim$3 mm/day. There was not revealed any influence of the concentration of TiO_2 impurity on the change of the solution’s pH and the saturation temperature. For the present study there were manufactured satellite samples cut out of the growth sectors {1 0 0} and {1 0 1}. They were shaped as thin plates with the dimensions $10 \times 10 \times 0.8\ mm^3$ and the faces oriented along the crystallographic axes. All the surfaces of the samples were finished by optical polishing. The photographs of the as-grown crystals with incorporated nanoparticles are shown in Fig. 1.

To find out the influence of TiO_2 nanoparticles on the growth of KDP crystal faces there was studied the crystal growth kinetics in the dynamic regime. For the crystal growth kinetics measurements there was used the laser-polarization–interference technique [31]. The dynamic crystal growth regime was provided by mixing of the solution using a magnetic stirrer with an interval of 20 s and a pause of 3 s. The seed of the crystal ($10 \times 5 \times 1\ mm^3$) fixed on the tip of a mercury thermometer was placed into a 40 ml thermostatted crystal-growth cell. At the initial stage the temperature in the crystal-growth cell was set several degrees above the saturation temperature (50 °C), then it was lowered at a constant rate of 0.75 °C/h (with an error of ±2%). All the investigated solutions were preliminarily filtered and overheated during three days at 80 °C at stirring.

2.2. X-ray diffraction analysis

The influence of nanocrystalline anatase particles on the structure perfection of the matrix was studied by High Resolution Three-Crystal X-ray Diffractometer (HRTCD) [32]. In this diffractometer the scheme of the arrangement of the monochromator crystals and the investigated sample $(n, n, -m)$ makes it possible to minimize the contributions of the wave and angular dispersions and to obtain diffraction reflection curves close to the theoretical ones, in approximation of dynamical scattering theory [32]. As structure perfection criteria, there were chosen the following parameters: the shape of rocking curve (RC), the RC Full Width at Half Maximum (FWHM) – $\overline{\beta}$, arcsec; the integral power of X-ray reflection I^R and the relative change of the crystal lattice parameters $\Delta d/d$. Such parameters were obtained in the Bragg geometry on reflection R_i and Laue geometry on reflection R_i and transmission T_i (R_i and T_i being the integral powers of the reflected and transmitted beams, respectively). This allowed to determine the integral coefficients of interference absorption μ_i and y_i in the dynamic approximation of “thick” crystal for which $i = T_i = R_i$ and $\mu t \geqslant 12$ (where t is the thickness of the investigated crystal and μ is the coefficient of normal photoelectric absorption). On 2–0.5 mm thick samples of the orientation {1 0 0} and {0 0 1} in Laue geometry on reflection and transmission there was studied anomalous X-ray transmission in the crystals.