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Linear and nonlinear optical properties of KDP crystals with incorporated $Al_2O_3{\cdot}nH_2O$ nanoparticles

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ABSTRACT

Optical and nonlinear optical properties of a novel composite system based on KDP single crystals with embedded nanoparticles of nanostructured oxyhydroxide of aluminum ($Al_2O_3{\cdot}nH_2O$, NOA), were studied. KDP crystals with NOA nanoparticles (KDP:NOA) possess high optical quality and homogeneity. Optical spectroscopy showed the presence of an absorption band at 270 nm caused by NOA nanoparticles incorporated in the KDP matrix. There was observed an enhancement of nonlinear refractive index and inversion of its sign in KDP:NOA crystals in comparison with nominally pure KDP crystals under excitation of picosecond laser pulses. The obtained results demonstrate that KDP:NOA is a promising composite material for optoelectronics and nonlinear optics.

1. Introduction

Potassium dihydrogen phosphate family crystals (KDP, DKDP, ADP) are among the materials most widely used in nonlinear optics, optoelectronics and photonics. Such crystals possess a unique set of properties, including wide transparency range, high laser damage threshold, and can be grown large-sized. This gives rise to their reasonable application as large aperture frequency converters of laser radiation and electrooptic switches in powerful laser systems for inertial confinement experiments.

As is known, for subpicosecond and femtosecond duration of laser radiation the efficiency of the ultra-intense frequency-conversion processes in KDP crystals, including second harmonic generation (SHG), is limited by nonlinear effects such as self- and cross-phase modulation (SPM, XPM) originating in the third-order nonlinear susceptibility $\chi^{(3)}$ [1,2].

The general approach to improve the quality of KDP single crystals and their frequency conversion efficiency is incorporation of various organic/inorganic "guest" subsystems into the crystalline matrix at the stage of growth [3–7]. However, non-isomorphic inclusions may cause essential nonlocal deformations of the crystal lattice [8]. Another possible way for solving the above-mentioned problem is the creation of nonlinear optical elements on the basis of nanophase composite materials, such as nonlinear optical dielectric matrix with incorporated metal oxide nanoparticles. This will provide efficient control of optical radiation flow (parametric amplification, SHG) due to the effects of nonlinear refraction and nonlinear absorption at nano-, pico- and femtosecond duration of pulsed laser irradiation. Investigation of the phenomena bound up with modulation of the refractive index of nanophase media and conversion of laser radiation frequency, will make it possible for promising researchers and engineers to apply new approaches for obtaining efficient harmonic generation.

The possibility to grow KDP single crystals with incorporated anatase (TiO_2 polymorph) nanocrystals (15 nm) was shown for the first time in Ref. [9]. The enhancement of frequency conversion efficiency was obtained in KDP:TiO_2 versus KDP single crystals due to the internal self-focusing effect of the pumping beam caused by the giant cubic nonlinear optical (NLO) response of the embedded nanoparticles (NPs) [6].

The next step was the incorporation of nanoparticles of nanostructured oxyhydroxide ($Al_2O_3{\cdot}nH_2O$, NOA) of aluminum into the crystalline matrix of KDP. The possibility to grow KDP single crystals with embedded NOA nanoparticles (KDP:NOA) was shown in Ref. [10]. The optical, NLO and photoluminescent properties of NOA as a promising material for different applications were studied in detail in [11–13]. NOA nanofibrils possess NLO response a few orders of magnitude higher in comparison with the response of bulk alumina [11]. The effect is due to resonant excitation of

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defect states at the developed NOA surface. Besides, the nonlinear optical and photoluminescent response was shown to be modified under thermal treatment of NOA nanofibrils [12,13]. Large specific surface and open porosity makes it possible to use NOA in catalysis, filtration of hot gases, immobilization of radioactive wastes, and as a matrix for proton-exchange membranes in fuel cells.

Thus, the incorporation of NOA NPs into the crystalline matrix of KDP is a promising approach to the design of novel composite systems on the base of dielectric matrices with controlled properties. The present work is aimed at optical and nonlinear optical characterization of KDP:NOA single crystals.

2. Experimental section

Pure KDP and KDP:NOA crystals were grown from aqueous solutions by the temperature reduction method onto $10 \times 10 \times 10\ mm^3$ point seed in 6 L crystallizers. The concentrations of background impurities of cations (Fe, Cr, Al, Pb, Mg, Mn etc.) in the initial KH_2PO_4 salt did not exceed 0.5–1 ppm. The starting temperature of the mother liquor was 50 °C, the solution was filtered through filters with a pore diameter of 0.05 μm to remove extraneous solid and colloidal particles. After filtration the solutions were overheated at 80 °C for a day.

NOA nanofibrils were prepared by oxidation of aluminum in wet atmosphere through mercury film at room temperature by Vignes, France [14]. The chemical composition of NOA is $Al_2O_3 \cdot nH_2O$, where $n = 3.5–3.6$. The as-obtained products are amorphous up to 870 °C, and their microscopic observation reveals that they consist of fibrils with a diameter of about 5 nm and a length of ~150 nm [14–16]. X-ray diffraction shows amorphous nature of NOA nanofibrils with three broad halos at $2\theta = 14°$, 34° and 48° (Fig. 1).

The NOA concentration (C) in KH_2PO_4 solution varied from 0.1 to 10 ppm in terms of KH_2PO_4 salt. Prior to the crystal growth the nanofibrils were subjected to ultrasonic treatment for an hour and then added to the mother liquor in the form of suspension at $T = 65$ °C. Rotation in “forward-stop-backward” regime during the growth run kept the NPs in the state of suspension. The crystal growth rate ranged between 1.5 and 3 mm/day and depended on the NOA concentration (Fig. 2). The optical studies were performed on the test samples with the dimensions $10 \times 10 \times 0.8\ mm^3$ and $10 \times 10 \times 10\ mm^3$ cut out from the {100} and {101} growth sectors (Z-cut) with polished (001) face.

The transmittance spectra in the UV–vis–NIR region were observed by a PE Lambda 35 recording spectrophotometer. In order to reveal the spectral peculiarities associated with the presence of NPs in the crystalline matrix, we measured the transmittance spectra of the growth solutions, grown crystals and dissolved crystals. We used the samples with the dimensions $10 \times 10 \times 10\ mm^3$ cut out from both growth sectors of the crystals. The solutions were prepared by the following procedure. The required weights of the nanofibrils dissolved in twice distilled water were subjected to ultrasonic treatment for 15 min and then added to KH_2PO_4 solution saturated at room temperature. The transmittance spectra were recorded immediately after the solutions preparation.

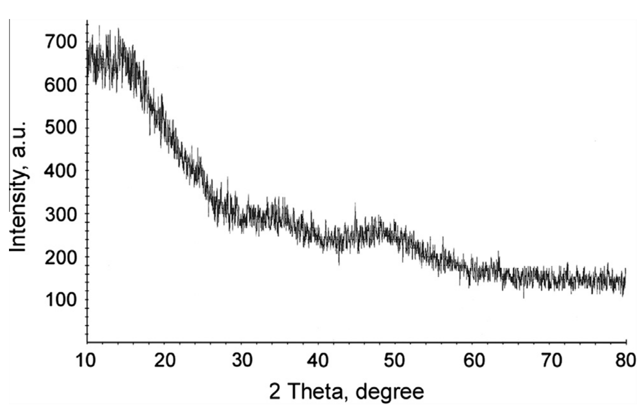

Fig. 1. XRD pattern of NOA nanofibrils.

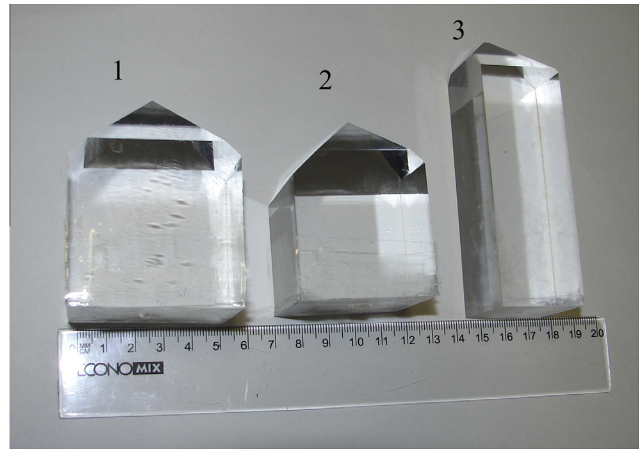

Fig. 2. NOA-doped KDP crystals grown from solution with different concentration of NOA: 1–0.1 ppm, 2–1 ppm and 3–10 ppm.

Optical distortion in the crystal was observed using a cone-shaped interference technique. The Z-cut sample was set between crossed polarizers and illuminated by a cone-shaped beam. The turn of the crystal around a normal to its surface was accompanied with the divergence of isogyres caused by anomalous biaxiality. The value of isogyre divergence (the angle $2V$) defined the extent of optical inhomogeneity. The measurements were performed for the Z-cut plates with a thickness of 10 mm and a width from 30 to 60 mm.

The impact of the incorporated NOA subsystem on the nonlinear optical response of KDP:NOA composite system was studied using the technique of spatial profile analysis under the self-action of single laser pulses of picosecond range at 1064 nm wavelength. The technique was approved while investigating nanoporous anatase layers, anisotropic mesoporous silicon films [17,18], as well as the subsystems of organic xylenol orange dye and TiO_2 NPs (anatase modification) in KDP crystalline matrix [5,19]. In KDP:TiO_2 composite system this revealed the manifestation of giant NLO response of anatase nanoparticles and its impact on the enhancement of the second harmonic generation efficiency due to internal self-focusing of the pumping beam.

The beam with TEM_{00}-mode spatial distribution of mode-locked Nd:YAG laser (42 ps FWHM, 5 Hz repetition rate) was focused onto the sample using a converging lens ($f = 11$ cm). The characteristic diameter of the laser beam on the sample was on the order of 1 mm and remained unchanged over the experiment. The incident intensity was increased up to 250 MW/cm^2 by neutral attenuator with a transmittance range from 1% to 50%. The energy transmitted through the sample (the so-called total transmittance) and the one passed through the diaphragm in the far field (on-axis transmittance) versus laser intensity, were registered. Their variations are caused by photoinduced changes of the absorption and the refractive index, respectively. The experimental procedure and the technique of estimation of the cubic NLO susceptibility imaginary and real parts are described in detail in [17].

The bulk laser-induced damage threshold (LIDT) was measured on well polished samples obtained in the above experiments with a