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Nonlinear optical response of the KDP single crystals with incorporated TiO_2 nanoparticles in visible range: effect of the nanoparticles concentration

***A.S.Popov*[1], *A.V.Uklein*[1], *V.V.Multian*[1], *I.M.Pritula*[2], *P.I.Budnyk*[1], *O.Kh.Khasanov*[3], *V.Ya.Gayvoronsky*[1]**

[1]Institute of Physics, National Academy of Sciences of Ukraine, 46 Nauki Ave., 03028 Kyiv, Ukraine
[2]Institute for Single Crystals, National Academy of Sciences of Ukraine, 60 Nauki Ave., 61001 Kharkiv, Ukraine
[3]Scientific-Practical Material Research Centre, National Academy of Sciences of Belarus, 19 Brovki Str., 220072 Minsk, Belarus

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Nonlinear optical response of KDP single crystals with incorporated TiO_2 nanoparticles (NPs) was studied within the self-action of picosecond laser pulses at 532 nm and second harmonic generation at 800 nm femtosecond laser pulses pump. The optical characterization of the composites KDP:TiO_2 was provided by elastic scattering indicatrices analyzes at 1064 nm. It was shown the significant reduction of the elastic scattering and self-action effects efficiencies in TiO_2 NPs doped KDP single crystals cut from pyramidal growth sector. The effect was attributed to the reduction of the non-controlled impurities concentration in the KDP:TiO_2 due to the NPs incorporation. The enhancement of second harmonic generation efficiency at about 60 % for pyramidal and 35 % for prismatic growth sectors was observed in composite crystals versus the nominally pure KDP matrix within the femtosecond pulses excitation at 800 nm. The obtained results indicate high potential for utilization of the KDP:TiO_2 single crystals in light frequency conversion.

Keywords: potassium dihydrogen phosphate (KDP), second harmonic generation, elastic optical scattering, nonlinear optical response.

Исследован нелинейно-оптический отклик монокристаллов KDP с инкорпорированными наночастицами (НЧ) TiO_2 при самовоздействии пикосекундных лазерных импульсов на длине волны 532 нм и генерации второй гармоники при возбуждении фемтосекундными лазерными импульсами на длине волны 800 нм. Для оптической характеризации композитов KDP:TiO_2 проведено исследование индикатрис упругого оптического рассеяния на длине волны 1064 нм. Показано значительное уменьшение эффективности упругого рассеяния и эффектов самовоздействия в монокристаллах KDP с инкорпорированными НЧ TiO_2, вырезанных из пирамидального сектора роста. Эффект объясняется уменьшением концентрации неконтролируемых примесей в KDP:TiO_2 вследствие инкорпорирования НЧ. Наблюдалось повышение эффективности генерации второй гармоники до 60 % в пирамидальном и 35 % в призматическом секторах роста в композитных кристаллах по сравнению с номинально чистой матрицей KDP при возбуждении фемтосекундными импульсами на длине волны 800 нм. Полученные результаты указывают на высокий потенциал использования монокристаллов KDP:TiO_2 в качестве эффективных преобразователей частоты.

Нелінійно-оптичний відгук монокристалів KDP з інкорпорованими наночастинками TiO_2 у видимому діапазоні: вплив концентрації наночастинок. *О.С.Попов, А.В.Уклеін, В.В.Мультян, І.М.Притула, П.І.Будник, О.Х.Хасанов, В.Я.Гайворонський.*

Досліджено нелінійно-оптичний відгук монокристалів KDP з інкорпорованими наночастинками (НЧ) TiO_2 при самовпливі пікосекундних лазерних імпульсів на довжині хвилі 532 нм і генерації другої гармоніки при збудженні фемтосекундними лазерними імпульсами на довжині хвилі 800 нм. Для оптичної характеризації композитів KDP:TiO_2 проведено дослідження индикатрис пружного оптичного розсіювання на довжині хвилі 1064 нм. Показано значне зменшення ефективності пружного розсіювання і ефектів самовпливу у монокристалах KDP з інкорпорованими НЧ TiO_2, що були вирізані з пірамідального сектора росту. Ефект пояснюється зменшенням концентрації неконтрольованих домішок у KDP:TiO_2 внаслідок інкорпорування НЧ. Спостерігалося підвищення ефективності генерації другої гармоніки близько 60 % у пірамідальному і 35 % у призматичному секторах росту у композитних кристалах у порівнянні з номінально чистою матрицею KDP при збудженні фемтосекундними імпульсами на довжині хвилі 800 нм. Отримані результати вказують на високий потенціал використання монокристалів KDP:TiO_2 в якості ефективних перетворювачів частоти.

1. Introduction

The potassium dihydrogen phosphate (KDP, KH_2PO_4) single crystals are widely used for optoelectronics and nonlinear optics application due to their extremely high structural and optical perfection. Nevertheless, the drawback of these crystals is low magnitude of d_{36} nonlinear coefficient which determines second harmonic generation (SHG) efficiency in comparison to borate crystals family. An effective method to improve properties of the dielectric crystals is organic/inorganic admixtures incorporation during the growth process. Nowadays studies are targeted to design composite materials based on KDP matrix with incorporated organic impurities [1–4] and inorganic nanoparticles (NPs) [5–7]. Variation of the NPs origin and size, their consolidation (isolated particles, linear and 3D structures) makes it possible to adapt the material to different application felds [8]. In order to design novel lasing media the KDP matrix has been already used as a host for dielectric SiO_2 [9] and semiconductor CdTe NPs [10].

The efficient results were achieved for the nanocomposites based on KDP crystals with incorporated TiO_2 NPs in anatase modification. The obtained improvement of the KDP matrix cubic NLO response in near IR range due to the NPs incorporation resulted in significant enhancement of the SHG (20–70 %) [5, 11, 12], sum-frequency (~ 2 times) [12] and supercontinuum generation (~ 5 times) [13] efficiencies.

In this paper we study the effect of the TiO_2 NPs incorporation on the scattering properties and NLO response of nanocomposites KDP:TiO_2. The preliminary results of SHG studies in KDP:TiO_2 under femtosecond laser excitation were discussed.

2. Experimental

Pure KDP and KDP crystals with incorporated TiO_2 NPs (10^{-5}–10^{-3} wt.%) were grown by the method of temperature reduction in the crystallizer (2000 g of KDP salt were dissolved in 5 L of twice distilled water). The growth solution was stirred at a velocity of 76 rpm. The saturation temperature was 51±0.1°C (σ^* ~ 2/3 %), the growth temperature ranged between 51 and 24°C and the mother liquor acidity was pH 4.1. The final size of the grown crystals was ~60×60×70 mm^3, the average growth rate ~3 $mm \cdot day^{-1}$ in both [001] and [100] directions. It was found no TiO_2 concentration impact on solution pH, saturation temperature and crystal morphology [14–16]. The experimental samples were cut from different growth sector in the form of thin plates 10×10×0.8 mm^3 perpendicular to the optical axis (Z-cuts) as it was shown in [6]. The samples notation, their thicknesses, NPs concentration in growth solution and NPs concentration in the grown crystals are presented in the Table 1. One can see that the NPs are preferentially captured by pyramidal (P) growth sector that was explained by the different surface charge of different growth sectors [17].

The self-action of picosecond laser pulses (42 ps FWHM, repetition rate 15 Hz) at 532 nm in KDP:TiO_2 crystals was studied within the laser beam spatial profile analysis in the far field [5]. The proposed method was successfully applied for the KDP:TiO_2 crystals study under pulsed laser excitation at 1064 nm [5, 15]. In this paper the obtained total and on-axis transmittance dependences are presented as the smoothed curves produced by local B-splines of measured data. Each curve corresponds to the ~ 5000 registered laser shots. The relative errors of the

Table 1. Samples notation, thicknesses, TiO_2 NPs concentration in growth solution, integral scattering losses ε_{scat} into forward hemisphere for the KDP:TiO_2 single crystals under the resonant excitation of the NPs defect states at 1064 nm and KDP crystalline matrix intrinsic defects at 532 nm

Sample	TiO_2 conc., wt. %	Thickness, mm	ε_{scat}(1064 nm), %	ε_{scat}(532 nm), %	ε_{scat}(1064 nm)/ ε_{scat} (532 nm)
P	–	0.81	0.5	1.0	0.50
P5	10^{-5}	0.75	0.3	1.7	0.18
P4	10^{-4}	0.76	0.4	2.5	0.16
Pr	–	0.83	0.6	1.1	0.54
Pr5	10^{-5}	0.78	1.2	1.7	0.71
Pr4	10^{-4}	0.75	0.8	1.3	0.62
Pr3	10^{-3}	0.81	0.7	2.8	0.25

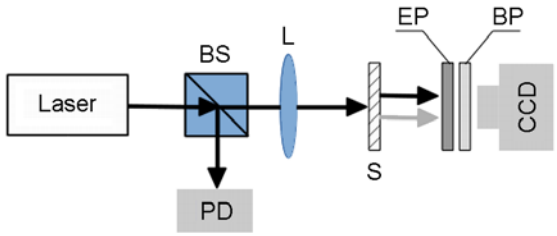

Fig. 1. Scheme of the experimental setup for the SHG efficiency measurements: PD — reference photodiode, BS — beam splitter, L — lens, CCD — CCD camera, EP, BP — edgepass and bandpass filters.

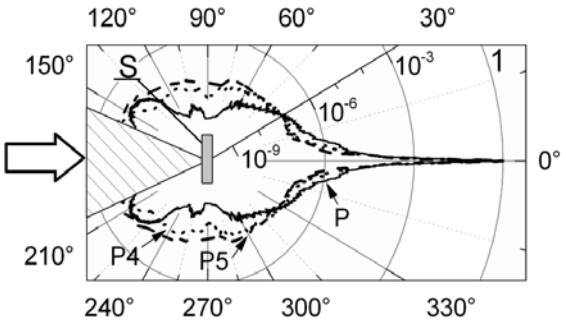

Fig. 2. Scattering indicatrix cross-section for KDP:TiO_2 single crystals cut from pyramidal growth sector under resonant excitation of TiO_2 NPs by CW laser radiation at 1064 nm wavelength. Samples notation are presented in Table 1.

curves do not exceed 0.2 % for the total and 1 % for the on-axis transmittance dependences, correspondingly.

The second harmonic generation in the crystals was studied within the pump of femtosecond laser pulses (200 fs FWHM, repetition rate 1 kHz) at 800 nm. The scheme of the experimental setup is presented in Fig. 1. The sample was positioned at the distance 9 from the focusing lens L with focal distance 11 cm. The SH signal readout was realized by CCD camera ATiK 16IC. In order to cut the fundamental radiation and extract SH signal the edgepass (EP) and bandpass (BP, 405 nm, 10 nm FWHM) filters was positioned before the CCD camera. The energy of the incident pump pulses was measured by photodiode PD.

3. Results and discussion

In order to study the optical quality of the KDP:TiO_2 crystals we measured the elastic optical scattering indicatrices at 1064 nm. The chosen wavelength is in the range of the TiO_2 NPs resonant excitation.

The typical scattering indicatrices cross sections for the samples cut from pyramidal (P) growth sector are presented in Fig. 2 in logarithmic scale. Propagation direction of the incident laser beam is shown with empty arrow. The sample is positioned in the center for better clarity. All data were normalized on the maximum scattering intensity magnitude for the nominally pure P crystal that is located at the 0° scattering angle and corresponds to the portion of photons that exhibited relatively small scattering impact. It can be seen that scattering indicatrices profiles are strongly dependent on TiO_2 NPs concentration in growth solution. From the obtained dependences the scattering losses ε_{scat} into forward hemisphere were estimated according to the approach described in [5]. The obtained results are presented in Table 1 and compared with the ones obtained for the same crystals at 532 nm. One can see that the incorporation of TiO_2 NPs results in scattering efficiency reduction for the crystals from P growth sector at 1064 nm (see Table 1). The effect can be explained by less non-controlled impurities concentration in the crystals with titanium dioxide [17, 18]. The obtained result is op-

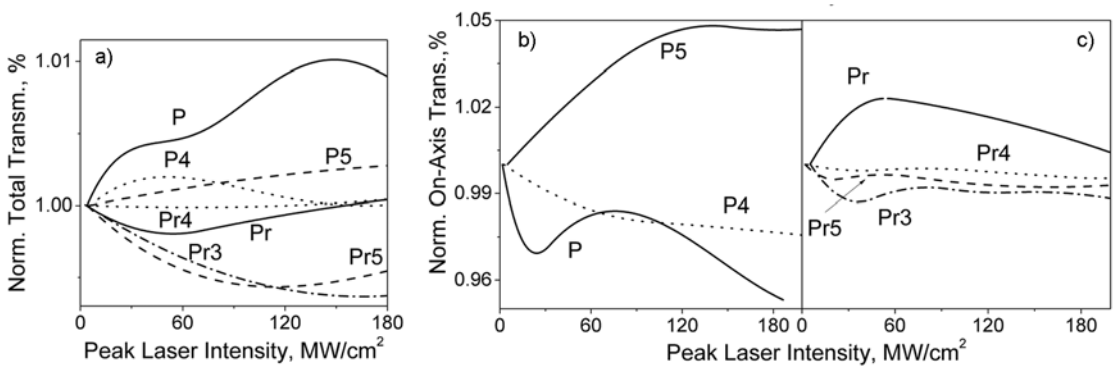

Fig. 3. The photoinduced variations of the total transmittance for the KDP:TiO_2 single crystals — (a); the photoinduced variations of the on-axis transmittance for the KDP:TiO_2 single crystals cut from pyramidal (b) and prismatic (c) growth sectors. The excitation was performed by the picosecond laser pulses at 532 nm. Samples notation is presented in Table 1.

posite to the observed ε_{scat} rise for the case of the resonant excitation of the KDP matrix intrinsic defects at 532 nm.

For the samples cut from Pr growth sector the scattering efficiency increase versus the nominally pure KDP crystal was shown. The rise of the NPs concentration results in ε_{scat} reduction that can arise due to the waveguide effect between the NPs layers.

In general, the obtained scattering losses at 1064 nm do not exceed 1 % that indicates high optical quality of the studied nanocomposites.

The ratio ε_{scat}(1064 nm)/ε_{scat}(532 nm) remains less than 0.71 for the studied samples (Table 1).

The NLO properties of the KDP and the KDP:TiO_2 single crystals were studied within the self-action of picosecond laser pulses at 532 nm. The excitation wavelength is overlapped with the intrinsic defects bands of localized and self-trapped hole polarons in the nominally pure KDP crystals [19].

The photoinduced variations of the normalized total transmittance for the samples are presented in Fig. 3a. One can see that even the nominally pure KDP matrix exhibit different NLO response in P and Pr growth sectors. For the sample P the photoinduced optical bleaching $\Delta\alpha(P) < 0$ was observed versus the photoinduced darkening $\Delta\alpha(Pr) > 0$ for the Pr one. The incorporation of the TiO_2 NPs into the KDP crystal results in the reduction of its absorptive NLO response efficiency in P growth sector. The effect can be explained by less non-controlled impurities concentration in the crystals with TiO_2 and consequently less concentration of the intrinsic defects in the KDP:TiO_2 nanocomposites. For the Pr growth sector the significant photoinduced absorption efficiency reduction was observed only for the Pr4 crystal.

In general, the photoinduced variations of the total transmittance for all studied samples do not exceed 1 %. It is less versus the previously observed 3 % within the picosecond laser pulses excitation at 1064 nm that corresponds to the resonant excitation of the TiO_2 NPs [15].

In comparison to the photoinduced absorption the photoinduced variations of the on-axis transmittance are more efficient. The dependences are presented in Fig. 3b and 3c for the samples cut from P and Pr growth sectors, correspondingly. For the nominally pure KDP matrix it was observed about 4 % reduction of the on-axis transmittance due to the self-defocusing effect in the P growth sector ($\Delta n(P) < 0$) versus the self-focusing induced 2 % rise in the Pr one ($\Delta n(Pr) > 0$) The observed different sign of the $\Delta\alpha$ and the Δn in different growth sectors can be used for the commercial KDP crystals certification. It should be noted that the mentioned effects saturates at about 60 MW/cm^2.

In the case of the P growth sector the incorporation of the TiO_2 NPs resulted in the refractive NLO response sign turn to the self-focusing for the sample P5 and significant reduction of the pronounced self-defocusing effect efficiency for the sample P4. For the Pr growth sector the self-defocusing effect was observed for all crystals with TiO_2.

The calculated Im($\chi^{(3)}$) and Re($\chi^{(3)}$) magnitudes for the peak intensity range <30 MW/cm^2 due to the approach described in [5] are presented in Table 2. One can see that in general the TiO_2 NPs incorporation results in reduction of the cubic NLO response of the KDP matrix. The effect can be

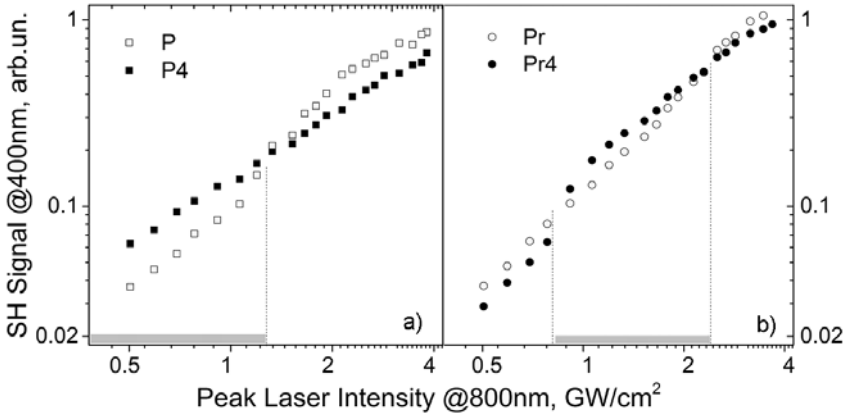

Fig. 4. The SHG signal in KDP:TiO_2 single crystals cut from pyramidal (a) and prismatic (b) growth sectors versus the pump peak intensity of femtosecond laser pulses at 800 nm. The dependences are presented in double logarithmic scale Samples notation is presented in Table 1.

Table 2. The real and imaginary parts of the cubic nonlinear optical susceptibility $\chi^{(3)}$ for KDP:TiO_2 single crystals with different TiO_2 NPs concentration

Sample	Re($\chi^{(3)}$), 10^{-11} esu	Im($\chi^{(3)}$), 10^{-13} esu
P/Pr	−3.1/1.1	−3.2/1.1
P5/Pr5	0.9/−0.3	−0.3/1.3
P4/Pr4	−0.6/−0.1	−1.2/0.1
−/Pr3	−/−0.8	−/1.8

attributed to the reduction of the intrinsic defects concentration in the KDP:TiO_2 nanocomposites. The most efficient reduction was observed for the crystals P4 and Pr4.

According to the results, the studies of the harmonic generation were performed. The SH signal dependences (without phase matching conditions) for the nominally pure crystals (P, Pr) and KDP:TiO_2 (P4, Pr4) under femtosecond laser excitation at 800 nm are presented in Fig. 4 in double logarithmic scale. The measurements were provided for chosen peak laser intensity range 0.4–4 GW/cm^2 that was below the experimentally obtained supercontinuum generation threshold ~ 5 GW/cm^2 in KDP single crystals at 800 nm. It was shown that the incorporation of anatase nanoparticles into KDP crystalline matrix leads to the SHG efficiency modification. For the KDT:TiO_2 samples it enhances at about 60 % for P and 35 % for Pr growth sectors versus the pure KDP crystals in the certain pump peak intensity ranges 0.4–1.3 GW/cm^2 and 0.8–2.3 GW/cm^2, correspondingly (see Fig. 4). Different character of the SHG dependences for P and Pr growth sectors of KDP:TiO_2 crystals can be related to the different TiO_2 NPs concentration (see Table 1) [17].

Recently the SHG studies for the "thick" (~ 1 cm) KDP:TiO_2 crystals within phase-matching conditions under the excitation of picosecond (42 ps) laser pulses at 1064 nm demonstrated [5] about 70 % of the SHG efficiency enhancement [5, 11]. The effect was explained by the observed internal self-focusing effect in the nanocomposite produced by the giant cubic NLO response of the anatase nanocrystals embedded into the matrix and its impact on the proton subsystem of the KDP crystal. For the "thin" (~0.8 mm) samples it was shown no significant change of the quadratic nonlinear coefficient due to the NPs incorporation that also did not vary with NPs concentration [20]. The obtained SHG efficiency reduction at about 2 times for Pr4 crystal versus the pure Pr one was explained by resonant absorption of SH wavelength energy and two-photon absorption of the fundamental one by TiO_2 NPs. The studied "thin" samples have no significant effect of the high-order NLO responses on the SHG efficiency.

For the case of the excitation at 800 nm, the SH wavelength corresponds to the energy state of the KDP matrix intrinsic electronic defects that are related to the interstitial hydrogen atoms H^0 [19]. We suggest that observed SHG efficiency enhancement for the P4 and Pr4 crystals can be attributed to the resonant excitation of the defects, being effected by interaction with TiO_2 NPs.

According to the mentioned, we suggest the further studies of the SHG efficiency for the thicker crystals in the field of femtosecond range laser pulses at 800 nm in order to provide the self-action effects impact. In this case the samples thicknesses

should not exceed 6 mm in order to avoid the group velocity dispersion impact for corresponding experimental conditions. The preliminary studies for the ~ 5 mm KDP:TiO_2 crystals with the same NPs concentration from P growth sector have shown about 5 times gain of the supercontinuum generation efficiency versus the pure matrix within the femtosecond range pulses excitation at 1240 nm at higher peak intensities ~ 250 TW/cm^2 [13]. The NPs incorporation into dielectric matrix also can provide the terahertz radiation generation efficiency enhancement [21].

4. Conclusions

The characterization of nanocomposites based on KDP single crystals with incorporated TiO_2 nanoparticles was performed by elastic scattering indicatrices and NLO response analyzes. It was shown the reduction of the scattering losses at 1064 nm in forward hemisphere due to the TiO_2 NPs incorporation at concentrations 10^{-5}–10^{-4} wt.% in pyramidal growth sector versus the nominally pure KDP matrix. The effect was explained by less non-controlled impurities concentration in the crystals with TiO_2. The scattering losses did not exceed 1% that indicates high optical quality of the studied nanocomposites.

The NLO response analysis has revealed the opposite signs of the photoinduced absorption and refractive index variations in the KDP single crystals cut from different growth sectors under picoseconds laser pulses at 532 nm: negative ones for pyramidal ($\Delta\alpha(P) < 0$ and $\Delta n(P) < 0$) and positive — for prismatic ($\Delta\alpha(Pr) > 0$ and $\Delta n(Pr) > 0$) growth sectors. The incorporation of TiO_2 NPs results in NLO response efficiency reduction and sign turn. The observed almost total compensation of the KDP matrix NLO response at NPs concentration 10^{-4} wt.% was attributed to the reduction of the intrinsic defects (potassium and hydrogen vacancies) due to the NPs incorporation.

The second harmonic generation efficiency for the KDP and the KDP:TiO_2 with 10^{-4} wt.% of NPs crystals was studied within the excitation of femtosecond range pulses at 800 nm without phase matching conditions. It was shown the SHG efficiency enhancement up to 60% for pyramidal and 35 % for prismatic growth sectors in pump intensity ranges 0.4–1.3 GW/cm^2 and 0.8–2.3 W/cm^2, correspondingly in the KDP:TiO_2 crystals versus the nominally pure KDP matrix.

The obtained results indicate high potential for utilization of the KDP:TiO_2 composite single crystals as light frequency converters with enhanced efficiency.

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References

1. J.B.Benedict, P.M.Wallace, P.J.Reid et al., *Adv. Mater.*, **15**, 1068 (2003).
2. M.Rifani, Y.-Y.Yin, D.S.Elliott et al., *J. Am. Chem. Soc.*, **117**, 7572 (1995).
3. G.Li, G.Zheng, Y. Qi et al., *High Pow. Laser Sci. and Eng.*, **1**, 006 (2014).
4. K.Boopathi, P.Rajesh, P.Ramasamy et al., *Opt. Mat.*, **35**, 954 (2013).
5. V.Ya.Gayvoronsky, M.A.Kopylovsky, M.S.Brodyn et al., in: Nanomaterials Imaging Techniques, Surface Studies, and Applications, Edition: Springer Proc. Phys., v.146, Springer, New York, USA (2013), p.349.
6. A.S.Popov, A.V.Uklein, V.V.Multian et al., *Opt. Commun.*, **379**, 45 (2016).
7. I.M.Pritula, A.V.Kosinova, D.A.Vorontsov et al., *J. Cryst. Growth*, **355**, 26 (2012).
8. H.I.Elim, W.Ji, A.H.Yuwono et al., *Appl. Phys. Lett.*, **82**, 2691 (2003).
9. E.B.Rudneva, V.L.Manomenova, A.E.Voloshin et al., *Crystallogr. Rep.*, **51**, 142 (2006).
10. A.Bensouici, J.L.Plaza, O.Halimi et al., *J. Optoelectron. Adv. Mater.*, **10**, 3051 (2008).
11. V.Ya.Gayvoronsky, M.A.Kopylovsky, M.S.Brodyn et al., *Laser Phys. Lett.*, **10**, 035401 (2013).
12. L.A.Golovan, G.I.Petrov, V.Ya.Gayvoronsky et al., *Laser Phys. Lett.*, **11**, 0755901 (2014).
13. L.A.Golovan, I.A.Ozheredov, A.P.Shkurinov et al., in: Abstr. Int. Conf. Coherent Nonl. Opt. (ICONO), Moscow, Russia (2013).
14. I.Pritula, V.Gayvoronsky, M.Kopylovsky et al., *Functional Materials*. **15**, 420 (2008).
15. I.Pritula, V.Gayvoronsky, M.Kolybaeva et al., *Opt. Mat.*, **33**, 632 (2011).
16. V.G.Grachev, I.A.Vrable, G.I.Malovichko et al., *J. Appl. Phys.*, **112**, 014315 (2012).
17. V.G.Grachev, R.Tse, G.I.Malovichko et al., *J. Appl. Phys.*, **119**, 034301 (2016).
18. I.M. Pritula, Y.N. Velikhov, in: R.B.Lal, D.O.Frazier (Eds.), Proc. SPIE, v.3793 (1999), p.202.
19. I.N.Ogorodnikov, V.Y.Yakovlev, B.V.Shulgin et al., *Phys. Solid State*, **44**, 880 (2002).
20. V.Ya.Gayvoronsky, M.A.Kopylovsky, V.A.Yatsyna et al., *Functional Materials*, **19**, 54 (2012).
21. O.Khasanov, O.Fedotova, G.Rusetsky et al., in: Abstr. Int. Conf. Coherent Nonl. Opt. (ICONO), Minsk, Belarus (2016).