GROWING $KTiOPO_4$ CRYSTALS AND STUDYING THEIR CHARACTERISTICS

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$KTiOPO_4$ *(KTP) monocrystals were grown from the polyphosphate multicomponent fluxes following Czochralski method with the rate of* 2.8 *to* 7 mm *per day. Crystals, grown with the pulling rate less than* 5.2 mm *per day, have radiant resistance up to* 3 GW/cm^2 *for a pulse of* 20 ns *duration. The conductance was* $4\cdot10^{-11}\ \Omega^{-1}\ cm^{-1}$ *along Z axis and less than* $1\cdot10^{-12}\ \Omega^{-1}\ cm^{-1}$ *along X and Y axes. The absorption coefficient at* 1.064 μm *was below* $1\cdot10^{-4}\ cm^{-1}$. *The coefficient of the second harmonic generation (*1.064 μm → 0.532 μm*) for the working element with* 10×10×7.7 mm^3 *overall dimensions reached* 70% *with the incident radiant flux density about* 10 MW/cm^2. *Maximum energy of the radiation converted reached* 1 J *per pulse at* τ = 20 ns *and* f = 20 Hz. *The absorption peaks at* 3585 cm^{-1} (2.8 μm) *that are related to* OH^- *groups were not observed in the IR spectrum. The crystals obtained are as good as those grown using the hydrothermal method as concerning their performance characteristics.*

$KTiOPO_4$ (KTP) monocrystals were grown from the polyphosphate multicomponent fluxes[1] by Czochralski method, the dimensions of boules grown reached 60×60×35 mm^3. The rate of seed pulling varied from 2.8 to 7 mm per day along the X axis. Temperature gradients in melt and air as well as the rate of seed rotation were chosen depending on the rate of seed pulling. One cycle of growing lasted, on the average, 6–10 days; and we succeeded in growing crystals with the size sufficient for making elements with overall dimensions up to 15×15×15 mm^3 for Nd:YAG laser radiation conversion into the second harmonic (1.064 → 0.532 μm). Shown in Fig. 1 is the map of the plate with 35×41×5.4 mm^3 size cut at an angle of 22.5° to the X axis. The measurements were carried out on the conversion of Nd:YAG laser radiation into the second harmonic.

It was found that crystals grown with the pulling rate greater than 5.2 mm per day tend to store admixtures and have the optical resistance about 1 GW/cm^2 in a volume, whereas for crystals grown with the pulling rate below 5.2 mm per day the radiant resistance reaches 3 GW/cm^2 for a pulse of 20 ns duration.

The conductance, s, was measured using specimens of 5×5×5 m^3 size, and it is $4\cdot10^{-11}\cdot\Omega^{-1}\ cm^{-1}$ for Z axis and less than $10^{-12}\cdot\Omega^{-1}\ cm^{-1}$ for X and Y axes.

Optical absorption at 1.064 μm was measured in the following way. Radiation from a Nd:YAG laser with pulse duration τ = 100 μs (laser operated in the free generation mode) was focused onto a specimen 7.7 mm long. Simultaneously, radiation from a He-Ne laser passed through a crystal. As a result of heating due to absorption in the Nd:YAG laser beam caustic, scattering of He-Ne laser radiation from the heated area was observed. Measuring the intensity of scattered radiation from He-Ne laser, it is possible to find the size of thermal lens of the Nd:YAG laser focal caustic and to reconstruct, after calibration, the value of absorption. The absorption coefficient of crystals under study being measured did not exceed $1\cdot10^{-4}\ cm^{-1}$ at 1.064 μm.

The characteristics of laser radiation conversion into the second harmonic were measured using a flash-lamp pumped Nd:YAG laser with the diffraction limited divergence (operating wavelength 1.064 μm, pulse repetition rate 20 Hz, pulse duration 20 ns, beam diameter 8 mm). The coefficient of the second harmonic generation was measured using a working element 10×10×7.7 mm^3 in size and it reached 70% at the incident radiant flux density about 10 MW/cm^3. Stable operation of the converter was observed at the energy per pulse up to 1 J and the average power of the radiation converted up to 20 W (we did not conduct tests at higher power).

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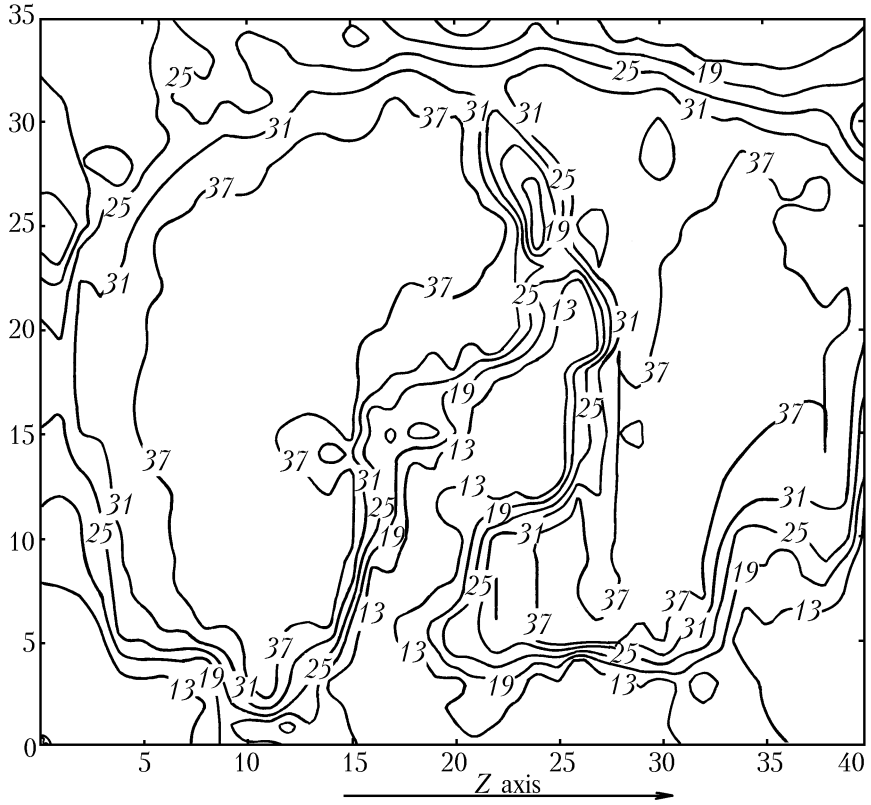

FIG. 1. Map of the KTP plate constructed with respect to Nd:YAG laser radiation (1.064 μm) *conversion into the second harmonic.*

To study UV spectra, we used KTP specimens cut out normally to the Z axis of a crystal 10×10×2 mm^3 in size. The UV spectra were recorded using a Specord-M40 spectrophotometer (300–900 nm). IR spectra were recorded at 77 and 295 K (KTP powder was tabletted in potassium bromide) using an IKS-29 spectrophotometer in the spectral range 400–4000 cm^{-1}. Gamma-irradiation was performed from a Co source (dose rate ~ 0.02 MGy/hour).

Absorption in the IR was measured for two specimens 6 mm thick cut out of crystals grown with the rate of 5.1 and 5.6 mm per day. Specimen No. 2 (5.6 mm per day) showed absorption peaks at 3585 cm^{-1} (2.8 μm) which are related to OH^- groups fixed at defects (their concentration was 12–18 ppm). In the spectrum of specimen No. 1 (5.1 mm per day) there were no such peaks, and, correspondingly, OH^- groups were not revealed.

Qualitative comparison of IR spectra obtained at T = 77 and 295 K showed their identity in the number of bands and the intensity pattern that allowed us to assume the crystals to have the same structure at these temperatures. Splitting observed in some bands is of resonance character. Exposure to γ-radiation gives rise to a new strong absorption band at 1330–1380 cm^{-1}. The nature of this band is under study now. Preliminary assignment of the rest IR bands is presented in Table I.

TABLE I. Assignment of IR absorption bands of KTP crystal.

Wavenumber, cm^{-1}, at $T_{295\ K}$	Intensity, conventional units	Assignment[2]
1125	weak	ν_{as} PO_4
1105	weak	ν_{as} PO_4
1053	weak	ν_{as} PO_4
1028	weak	ν_{as} PO_4
1003	weak	ν_{as} PO_4
975	weak	ν_s PO_4
820	medium	valent bonds Ti–O
785	medium	valent bonds Ti–O
710	weak	valent chain –Ti–O–
640	weak	δ_{as} PO_4
595	medium	δ_{as} PO_4
555	medium	δ_{as} PO_4
500	medium	δ_s PO_4
485	medium-strong	TiO_6
465	medium-strong	TiO_6
430	strong	PO_4 – ?
405	strong	TiO_6 (deform. O–Ti–O bridges)

Shown in Fig. 2 are the UV absorption spectra of KTP monocrystals without (curve *1*) and with (curve *2*) exposure to γ-radiation dose of about 1 MGy. Studying crystals grown under different regimes has shown that intensity of the background and color centers being formed can vary significantly. The results shown in Fig. 2 correspond to the highest quality crystals grown with the rate of 5.1 mm per day. As to the crystals of lower quality, after exposure to γ-radiation a nonuniform coloring of a volume is observed. In this case color centers being formed are concentrated near block sides and other defects of growing.

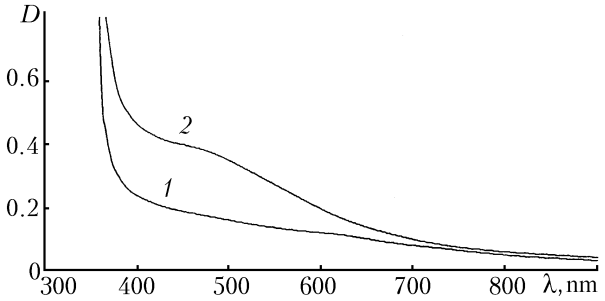

FIG. 2. UV absorption spectra of KTP monocrystals at 295 K *without (1) and with (2) exposure to γ-radiation.*

Increase in the absorbed dose of radiation above 0.5–1 MGy does not result in change in optical properties within 300–900 nm spectral region. Figure 3 shows the optical thickness D of irradiated crystal as a function of the dose absorbed. This dependence is characteristic of crystals with a great radiative resistance.[3] In this case the initial section of the curve describes the kinetic of radiation-chemical processes at impurity or defect places, and the end of section is characterized by the crystal resistance to radiation. Therefore, the quality of a crystal can be indirectly judged from the value of optical thickness and the period of reaching the stationary state under exposure. Color centers induced are unstable and can be baked out at a room temperature.

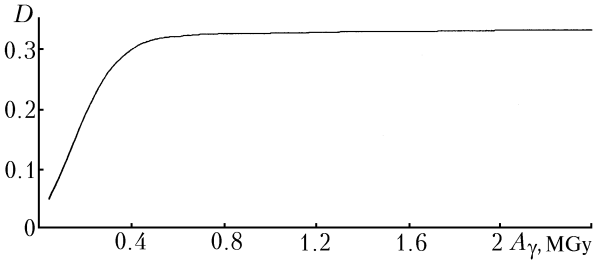

FIG. 3. Kinetics of the color centers storage vs. the absorbed dose of radiation.

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