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Methods of optical absorption reduction in irradiated KDP single crystals containing arsenic ions

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The processes of disappearance of radiation defects under thermal, laser, and ionizing irradiation annealing in gamma-irradiated potassium dihydrogen phosphate crystals containing arsenic ions have been investigated using electron paramagnetic resonance and optical spectroscopy. It has been found that the disappearance of some types of defect results in optical absorption reduction in crystal. Basing on the spectroscopic measurements, the possibilities, advantages and drawbacks of different crystal treatment methods including the above-mentioned kinds of annealing, have been determined. The optimal conditions of the crystal treatment have been determined.

В гамма-облученных кристаллах дигидрофосфата калия, содержащих примесные ионы мышьяка, с помощью электронного парамагнитного резонанса и оптической спектроскопии исследованы процессы исчезновения радиационных дефектов при термическом, лазерном и радиационном отжиге. Установлено, что исчезновение определенных типов дефектов приводит к уменьшению оптического поглощения в кристаллах. На основе спектроскопических измерений определены возможности, достоинства и недостатки различных способов обработки кристаллов, включающих указанные выше разновидности отжига. Определены оптимальные условия обработки кристаллов.

For the development of laser systems and other quantum electronics devices operated under short-wave laser and ionizing irradiation conditions, radiation-resistant crystals are necessary. The use of potassium dihydrogen phosphate KH_2PO_4 (KDP) crystals in laser systems and in electronics devices operating in ionizing irradiation conditions [1] requires a high stability of the crystal matrix and its optical characteristics against various kinds of irradiation.

The radiation-induced defects formed in defect-free KDP crystals are short-living at room temperature [2]. That is why at nearly-room temperatures, the crystal structure is radiation-resistant. In the presence of impurities, long-living defects are formed in the crystals. For example, Cu, Co, As, Al, Si, etc. ions result in stabilization of radiation-induced paramagnetic centers [3, 4–6] being holes on the p-orbital of oxygen ions. The hole-like centers influence the crystal optical absorption in the ultraviolet (UV) spectral range [5].

Considerable radiation-induced absorption is associated with the presence of arsenic impurity ions. During the growing of KDP crystals, arsenic ions enter easily the anionic sublattice substituting isomorphically for phosphorus ions in the crystal structure. Under irradiation, free radicals are formed in such crystals [7–10]. These radicals result in appearance of absorption bands in the UV spectral region.

The investigation results [5, 7–10] show that many undoped KDP crystals intended for laser engineering contain ^{75}As impurity that causes the radiation resistance reduction of KDP crystals. The arsenic impurity results in aging processes in crystals under

UV irradiation. This is evidenced by the formation of arsenic-containing free radicals under UV irradiation (mercury lamp). Hence, the arsenic impurity causes lowering of the radiation resistance of KDP crystals and restricts the crystal operation duration in laser devices.

First of all, the radiation stability of the KDP crystals can be enhanced by reducing the arsenic concentration in the initial materials being used to grow the crystals.

Thermal, laser and ionizing radiation treatment based on annealing of radiation damages [1, 7–12] can reduce the optical density of the irradiated crystals. This makes it possible to reuse the radiation-damaged elements made from KDP single crystals in quantum electronics devices [1]. Thus, investigation of decay of the radiation-induced defects in the crystals under various kinds of treatment is a topical problem.

In the above-mentioned works, the crystals grown by different techniques and using different raw materials were studied. In [1, 11, 12, etc.], the nature of the radiation defects has remained unclear. This does not allow to compare the efficiency of various crystal treatment methods and results in uncertainty in applicability of these methods in each specific case.

The aim of this work was to investigate the advantages and drawbacks of the irradiated KDP single crystals treatment methods using electronic paramagnetic resonance (EPR) and optical spectroscopy.

The samples of undoped KDP crystals grown by solvent re-circulation [1] were used in this investigation. To measure the optical density, the crystal samples of $10\times12\times L$ mm^3 size, where $L = 10–46$ mm is the sample dimension along the crystallographic c-axis, were cut out of the pyramidal part of crystals. Dimensions of the EPR samples were $3\times3\times10$ mm^3. As determined by chemical analysis, the impurity concentrations of Pb, Si, Fe, Al, Ca elements were $5\cdot10^{-5}$, $2.7\cdot10^{-3}$, $1.8\cdot10^{-4}$, $2\cdot10^{-3}$, and $2.8\cdot10^{-3}$ wt. %, respectively. According to [13], the ^{75}As impurity amount in potassium dihydrogen phosphate solutions was about 10^{-4} to 10^{-3} wt. %. The crystal samples were irradiated with γ-rays of a ^{60}Co source in the 10^3–$3\cdot10^3$ Gy dose range. The crystals containing a minimal amount of arsenic-containing radicals produced by γ-rays (10^{16}–10^{17} cm^{-3}) were selected for the studies.

The crystal optical density D as a function of wavelength was measured using of a Specord M40 spectrophotometer in the range of 200–700 nm along the c-axis of the crystals. EPR spectra were measured by means of an IRES-1001 X-band spectrometer. The nature of the radiation defects was determined from the EPR spectra. The concentration of the radiation-induced paramagnetic defects was calculated by a double integration of the absorption curves in the EPR spectra.

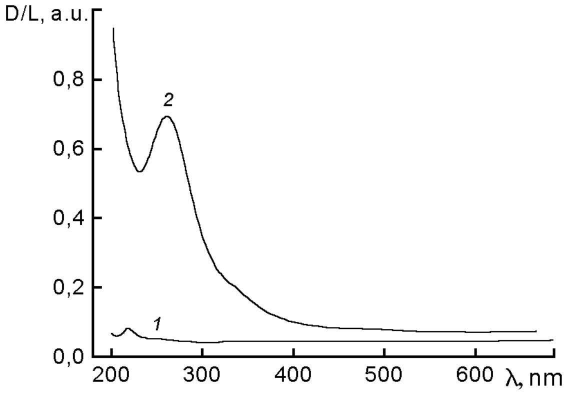

Fig. 1. Absorption spectra of unirradiated (*1*) and γ-irradiated (10^3 Gy) (*2*) KDP crystals.

The thermal treatment of the irradiated samples was carried out in the nitrogen atmosphere at 130–150°C. For the laser treatment of crystals, a nitrogen laser was used with 337 nm wavelength, 5 ns pulse width, 5–12 mW average power, 10 Hz pulse repetition rate. The γ-irradiation with a ^{60}Co source within 10^2–10^7 Gy dose range was used for the ionizing radiation treatment. The irradiation and spectroscopic measurements were carried out at room temperature.

The optical spectra of the unirradiated crystals do not contain any intense bands within a wide spectral range (Fig. 1). After irradiation, the intense resonant absorption bands arise in the optical spectra similar to those observed before in [1, 5, 7–12].

It is known [1] that programmed thermal annealing results in a considerable optical transparency increase of the radiation-damaged KDP crystals [1]. This phenomenon is usually associated with the thermal curing of radiation defects.

As is shown in [7–10], the optical transparency increase in irradiated KDP crystals containing arsenic impurity at the thermal annealing (Fig. 2) is caused by the disappearance of two broad optical absorption bands peaked at 260 and 350 nm which are associated with the AsO_4^{4-} and AsO_3^{2-} radical-ions, respectively.

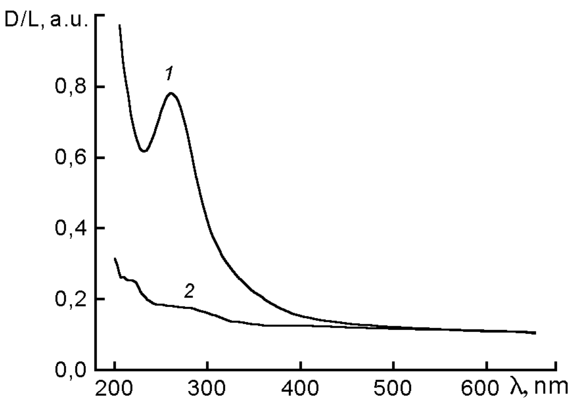

Fig. 2. Absorption spectra of γ-irradiated (10^3 Gy) KDP single crystal prior to (*1*) and after (*2*) thermal treatment at 130°C (8 h) and 145°C (6 h).

Isothermal annealing experiments carried out using EPR and optical spectroscopy confirmmake it possible to opitimize the annealing conditions of arsenic-containing radicals. The annealing duration at different temperatures resulting in the residual radical concentration not exceeding 10 % is presented in Table.

It is seen (Fig. 2) that after the two-stage isothermal annealing at 130 and 145°C a residual absorption remains associated with hole-like centers [5]. To remove it, higher annealing temperature (T_{an} ~ 180°C) near the phase transition are required. In this case, to prevent the crystal damage, rather complex annealing procedures [1] are to be applied including the low heating of crystals (3–0.3° C/h), stepwise lowering of the heating rate as approaching the isothermal annealing temperature and three-layer screening of samples.

Investigation of the dependences of the radiation-induced paramagnetic defects relative concentration on the thermal annealing duration shows that the thermal treatment provides a complete decay of the extrinsic AsO_4^{4-} and AsO_3^{2-} radiation defects contributing mainly to the radiation-induced optical absorption at 260 and 350 nm. The method drawbacks consist in that the extrinsic radiation defects appear again after repeated irradiation and the heat treatment at temperatures up to 150°C is ineffective for annealing of the several types of hole-like centers.

This work show that the laser annealing results in destruction of radiation-induced paramagnetic centers that absorb light at the laser radiation wavelength.

Table. Durations (min) of thermal annealing of free radicals in γ-irradiated KDP single crystals.

Type of free radical	Temperature of thermal treatment, °C				
	110	120	130	140	150
AsO_4^{4-}	2400	530	125	30	10
AsO_3^{2-}	–	–	–	>400	240

When the γ-irradiated ($3\cdot10^3$ Gy) KDP crystals are irradiated with nitrogen laser (power density W = 70 mW/cm^2 and laser fluence Φ ~ 500 J/cm^2) with 337 nm generation wavelength getting to the absorption band of the AsO_3^{2-} radical, the EPR signal from AsO_3^{2-} radicals decreases by a factor of 5. The higher W and Φ values result in the disappearance of the EPR spectrum of the AsO_3^{2-} radical. The absorption band peaked at 350 nm associated with the radical disappears.

Unfortunately, only several types of the radiation defects disappear after the nitrogen laser treatment as follows from the ESR spectra. Perhaps the use of lasers with higher frequencies is required to eliminate other types of defects. However, this may cause the formation of radiation defects. For example, irradiation of KDP crystals with the fourth harmonic of a neodymium laser (λ = 266 nm) causes the formation of the hole-like centers [4].

At irradiation of KDP crystals with electrons and γ-rays, the intensity decrease of the radiation-induced optical band at 260 nm was observed starting from a certain irradiation dose [11, 12]. However, this radiation effect was not established to be connected with specific defect types of radiation defects.

The high γ-irradiation doses (10^6–10^7 Gy) used in this work provide the complete disappearance of several absorption bands in KDP. This phenomenon has been found to be connected with the decay of the AsO_4^{4-} and AsO_3^{2-} radicals and HC1 and HC2 hole-like centers [5, 6]. A considerable increase in the optical transparency takes place at the doses corresponding to the AsO_3^{2-} radical disappearance. This effect associated with the transformation of paramagnetic centers [7–9] is applied in the method of ionizing radiation treatment of crystals [14]. In this method, the necessary irradiation dose D_c (a critical dose) is determined by means of EPR measurements. The critical dose corresponds to the disappearance of the AsO_3^{2-} radical bands. The D_c (that depends on the crystal growth conditions and the impurity composition) is specific for each individual series of crystals.

The long-wave wing of the 350 nm absorption band overlaps partially the visible spectral range. Therefore, the bleaching effect can be observed visually at some conditions of the irradiation.. The transparent unirradiated samples of KDP crystals acquire pale yellow colour at a dose of about 10^4 Gy, but they become transparent again after the ionizing radiation treatment at D_c dose. After the treatment, the crystal transparency approaches that of unirradiated crystals in the visible and long-wave UV spectral range (Fig. 3).

The optical characteristics of the radiation-treated crystals become radiation stable because the optical density changes very slowly at irradiation in the wide dose range. So, such crystals can be used in the devices operated under irradiation.

The γ-rays are most preferable for the ionizing radiation treatment. This kind of radiation does not influence essentially the crystal lattice, while a corpuscular irradiation such as proton one may damage the crystal surface [1].

The ionizing radiation treatment is reasonable in the case of low arsenic concentrations in the crystals. In this case, the AsO_3^{2-} centers decay at rather low doses which do not deteriorate essentially the crystal quality.

For the investigated KDP samples, the γ-ray D_c dose was $5\cdot10^6$ Gy. The fluences of electrons ($E = 8$ MeV) and neutrons (at the accompanying γ-irradiation) determined by extrapolating the dose dependences of radical relative concentration [14] were $\Phi_{ce} > 5\cdot10^{15}$ cm^{-2} and $\Phi_{cn} > 5\cdot10^{16}$ cm^{-2}, respectively.

The advantage of the ionizing radiation treatment is the possibility to obtain the KDP crystals with the radiation-stable spectral characteristics. The method drawbacks consist in that the method can be applied only to perfect and pure enough crystals; and the optical absorption does not disappear completely in the $250<\lambda<300$ nm range while increasing at $\lambda<240$ nm.

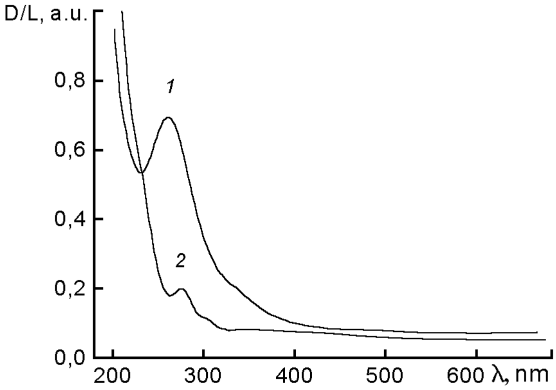

Fig. 3. Absorption spectra of γ-irradiated (10^3 Gy) KDP single crystal prior to (*1*) and after (*2*) ionizing radiation treatment with γ-ray ($5\cdot10^8$ Gy).

Thus, the thermal, laser and ionizing radiation treatments reduce the concentration of radiation-induced defects and the optical absorption associated with those in the irradiated KDP single crystals containing arsenic impurity. The choice of one or other treatment method depends on the specific application of the crystals. The isothermal treatment reduces the concentration of most types of the radiation defects contributing to the optical absorption. However, those appear again after repeated irradiation. The laser treatment at power density below the laser damage threshold decreases the concentration of defects responsible for the absorption bands coincident with the laser wavelength. However, it is to take into account that short-wave laser irradiation ($\lambda \le 266$ nm) results in formation of radiation defects increasing the optical absorbtion in crystals. The most effective way to enhance the radiation stability of the crystal optical characteristics is the ionizing radiation treatment which can be applied to crystals with a low concentration of defects (N~10^{16} cm^{-3}). The method can be used to reduce the radiation-induced optical absorption at the wavelengths of $\lambda > 250$ nm.

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Способи зменшення оптичного поглинання в опромінених монокристалах KDP, що містять іони миш'яку

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У гамма-опромінених кристалах дигідрофосфату калію, що містять домішкові іони миш'яку, за допомогою електронного парамагнітного резонансу і оптичної спектроскопії досліджено процеси зникнення радіаційних дефектів при термічному, лазерному та радіаційному відпалі. Встановлено, що зникнення визначених типів дефектів приводить до зменшення оптичного поглинання у кристалах. На основі спектроскопічних вимірювань визначено можливості, достоїнства та недоліки різних засобів обробки кристалів, що включають зазначені вище різновиди відпалу. Визначено оптимальні умови обробки кристалів.