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Origin of non-monotonic behaviour of electrical conductivity of potassium dihydrophosphate crystals depending on gamma-irradiation dose

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Investigated is the dependence of dc conductivity of undoped KDP crystals on the dose of gamma-irradiation and the temperature. At room temperature the value of conductivity changes non-monotonically with the dose of gamma-irradiation. At low irradiation doses it exponentially decreases as the irradiation dose rises. Then, after reaching the minimum at $1.2{\cdot}10^3$ Gy dose, the conductivity increases with further irradiation up to $2.0{\cdot}10^4$ Gy proportionally to the dose. The temperature dependences of the conductivity are measured in 15÷133 °C range. It is established that they obey the exponential law and are described by the Arrhenius relation. There are determined the conductivity parameters such as the activation energies and the pre-exponential factors. The analysis of the obtained results shows that at room temperature the non-monotonic dependence of electrical conductivity at gamma-irradiation is mainly bound up with the competition of two mechanisms of charge transfer: migration of proton vacancies and migration of protons along the interstices. The intrinsic mechanism related to the processes of thermal generation and migration of charge carriers dominates at temperatures above 85°C. The concentration of proton vacancies is determined, and its dependence on the gamma-irradiation dose is established.

Keywords: KDP single crystals, electrical dc conductivity, temperature dependences, crystal defects, gamma-irradiation effect

Природа немонотонної поведінки електропровідності кристалів дигідрофосфату калію в залежності від дози гамма-опромінення. *О.М.Левченко, І.М.Притула.*

Досліджено залежність питомої електропровідності на постійному струмі нелегованих кристалів KDP від дози гамма-опромінювання та температури. За кімнатної температури величина електропровідності змінюється немонотонно з дозою гамма-опромінення. При малих дозах опромінювання провідність зменшується зі зростанням дози за експоненційним законом, а після досягнення мінімуму при дозі $1{,}2{\cdot}10^3$ Гр при подальшому опроміненні до $2{,}0{\cdot}10^4$ Гр зростає пропорційно дозі. Виміряно температурні залежності електропровідності в інтервалі 15÷133 °C. Встановлено, що вони підпорядковуються експоненційному закону та описуються співвідношенням Арреніуса. Визначено параметри електропровідності – енергії активації та передекспоненційні множники. Аналіз отриманих результатів показує, що немонотонна залежність електропровідності при гамма-опромінюванні, яка спостерігається при кімнатній температурі, пов'язана в основному з конкуренцією двох механізмів перенесення заряду: міграцією протонних вакансій і міграцією протонів по міжвузлям. Власний механізм, пов'язаний з процесами термічної генерації та міграції носіїв заряду, домінує при температурах вище 85°C. Визначено концентрацію протонних вакансій та її залежність від дози гамма-опромінювання.

1. Introduction

Potassium dihydrophosphate (KH_2PO_4, KDP) single crystals are widely used in various electrooptical devices for control and conversion of laser radiation [1, 2]. A significant functional characteristic of these crystals is electrical conductivity. As shown in [3–8], it is greatly influenced by a number of factors, such as crystal structure defects, temperature and ionizing irradiation. The data on the effect of these factors on the conductivity are necessary for control and improvement of the crystal quality.

In the present work the conductivity of KDP was studied in the paraelectric phase. In this phase, the crystal has a tetragonal structure that consists of K^+ cations and $H_2PO_4^-$ anions. Each PO_4^{3-} group included in the anion is a tetrahedron connected to four neighboring tetrahedra through hydrogen bonds with a length of 2.48 Å [9].

Most of known models of electrical conductivity in KDP are based on proton transport. The existence of such a phenomenon is confirmed by the results of coulometric experiment and nuclear magnetic resonance (NMR) [10-14] that reveal the processes of proton migration in KDP family crystals.

The mechanisms of conductivity in KDP are mainly defined by the crystal lattice defects. As assumed in [3], the conductivity is bound up with migration of *D*– and *L*-defects (two protons in the double potential well between the two oxygen ions of the two neighbouring PO_4^{3-} tetrahedrons and the proton vacancy, respectively). The authors of [5] believe that the conductivity is due only to migration of *L*-defects. Nowadays this viewpoint is generally accepted [15–17].

The impurity conductivity in KDP depends on the impurity composition, hydrogen non-stoichiometry and the crystal part studied [6]. The cationic and anionic impurities increase the quantity of proton vacancies which participate in the process of charge transfer, whereas hydrogen non-stoichiometry leads to the appearance of an excess quantity of interstitial protons [6, 16, 17]. The presence of proton vacancies, or of excess protons in the crystal increases its conductivity. As reported in [16, 17], KDP conductivity is due not only to proton transfer, but also to migration of oxygen vacancies.

The intrinsic conductivity is bound up with two processes – thermally induced generation and migration of proton vacancies.

According to [3–5 et al.], KDP conductivity is defined by the expression:

$$\sigma = \sigma_{01} \cdot \exp(-E_{a1}/kT) + \sigma_{02} \cdot \exp(-E_{a2}/kT), \quad (1)$$

where σ_{01}, σ_{02} are the pre-exponential factors; E_{a1}, E_{a2}, conductivity activation energy.

The first term in (1) shows the contribution of the impurity conductivity related to migration of defects in the crystal structure. The second term describes the processes of intrinsic conductivity bound up with thermal generation and migration of intrinsic defects. As assumed in [5], the activation energy E_{a1} is related to the migration of proton vacancies, whereas $E_{a2} > E_{a1}$ is bound up with formation and migration of proton vacancies in a defect-free crystal. As a rule, the conductivity in the low-temperature ("impurity") region is mainly defined by the first term in (1) ("low-temperature conductivity"). In the high-temperature ("intrinsic") region it is described by the second term ("high-temperature conductivity") [5, 16]. Passing from the low-temperature to the high-temperature region of conductivity is characterized by a kink of the dependence $\lg\sigma(T) = f(1/T)$ [5] at a certain temperature.

Investigations of the influence of irradiation on the conductivity of KDP family crystals have yielded rather contradictory results. According to [7], at gamma-irradiation the conductivity increases, whereas, as found in [18], it decreases by almost an order of magnitude. In the present work there is studied the conductivity that nonmonotonically depends on gamma-irradiation dose.

The present work was aimed at finding out the origin of non-monotonic behaviour of the conductivity value at gamma-irradiation.

2. Materials and methods

In the study there were used nominally pure KDP single crystals grown by the method of solvent recirculation [19] (at a rate of 0.5–1 mm/day). Table 1 presents the results of chemical analysis of the crystals with the dimensions $4\times3\times3$ mm^3.

The value of conductivity at room temperature for the samples cut out from different parts of the same KDP crystal may differ by several orders of magnitude [6]. Therefore, in the present study we used the samples with close conductivity values cut out from the same part of the crystal. Prior to gamma-irradiation of the crystals their conductivity at room temperature was $(1.1\div1.5)\cdot10^{-11}$ S/cm.

Table 1. Results of impurity composition analysis of KDP single crystals.

Impurity content (wt.%)				
Pb	Si	Fe	Al	Ca
$2{\cdot}10^{-4}$	$3{\cdot}10^{-3}$	10^{-4}	$2{\cdot}10^{-3}$	$2{\cdot}10^{-3}$

The value of dc conductivity was determined by means of a teraohmmeter of E6-13A type, the error of the experiment was ±4–6%.

The conductivity depending on gamma-irradiation dose was measured at room temperature using conductive rubber electrodes to which a voltage of 100 V was applied. As a source of γ-radiation, there was used ^{60}Co. The crystals were subjected to γ-irradiation in 10^2–$2{\cdot}10^4$ Gy dose range at room temperature. To eliminate the scatter of the concentration and properties of the crystals over the volume of the sample, the dose dependences of the conductivity were measured on the same crystal sample during its sequential multiple irradiation.

To determine the conductivity parameters there were studied the temperature dependences obtained at heating of the crystals. They were measured in 15-133°C range using electrodes made of high-purity graphite for spectral investigations which covered the sample surface. The measurements were performed at 100 V voltage between the electrodes.

The influence of irradiation on the values of E_a and σ_0 was determined from the temperature conductivity dependences. Radiation defects in KDP crystals may disappear or change with increasing temperature. Therefore, the value of conductivity in the irradiated sample was measured at T < 100 ºC. In this case, the irradiation-induced conductivity changes were quite resistant to the influence of heat.

The conductivity parameters E_a and σ_0 were calculated from the slopes and the points of intersection of the temperature conductivity dependences with the axes in (lgσ, 1/kT) coordinates. For this purpose there was used the least squares method.

3. Results and discussion

Dose dependence of conductivity. The dose dependence of the conductivity measured in the present work is shown in Fig. 1. As follows from this figure, its peculiarity is a non-monotonic change in the conductivity value with increasing gamma-irradiation dose. At first, with low-dose irradiation (D <1.22·10^3 Gy) the conductivity value decreases reaching its minimum at

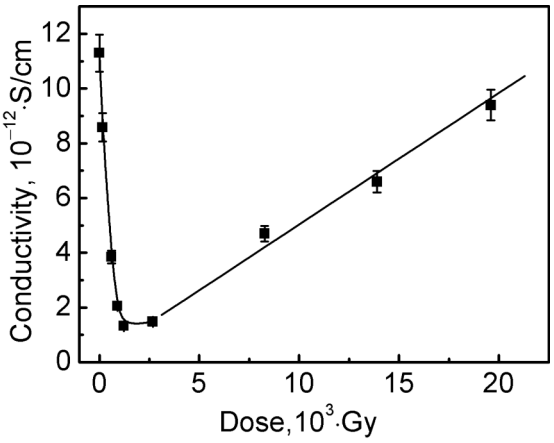

Fig. 1. Non-monotonic changes of electrical conductivity value in KDP single crystals depending on gamma-irradiation dose.

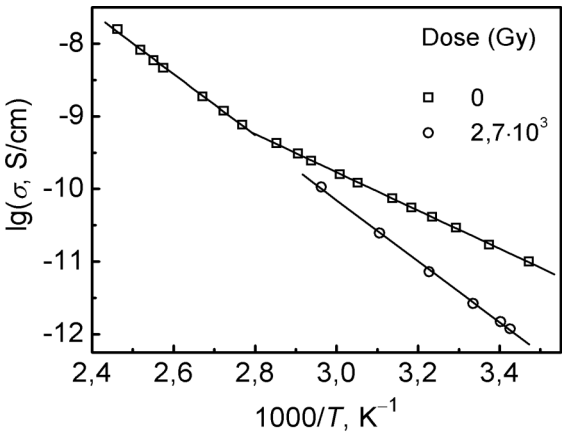

Fig 2.Temperature dependences of electrical dc conductivity of KDP single crystal before and after gamma-irradiation.

D≈1,22·10^3 Gy and becomes by an order of magnitude lower than the one in the unirradiated crystals. At further irradiation, it increases. In 2.7·10^3-2·10^4 Gy dose range the conductivity value is growing approximately proportionally to the absorbed dose.

Temperature dependences of conductivity. The temperature conductivity dependences of the unirradiated KDP crystals studied in the present work are characterized by a kink at T=85 ºC (see Fig.2).

After irradiation with the dose at which the conductivity reaches its minimum value this kink disappears. Thereat, the curve that corresponds to the irradiated sample precisely coincides with the high-temperature section of the curve for the unirradiated crystal. The temperature dependences also have no kink in case of higher irradiation doses in the studied temperature range, where irreversible changes

Table 2. Electrical dc conductivity parameters of non-irradiated and γ-irradiated KDP crystals.

Crystal	Dose, Gy	E_a, eV	lgσ$_0$, [σ$_0$]=S/cm	σ$_{RT}$[c], S/cm	*T*, °C	Notes	Ref.
KDP pure [a]	0	0.522±0.003	–1.87±0.06	$1.4\cdot10^{-11}$	<85	σ$_\perp$ [d]	This work
KDP pure [b]	0	0.835±0.024	2.54±0.26	$1.5\cdot10^{-12}$	>85	σ$_\perp$	This work
KDP pure [a]	$2.7\cdot10^3$	0.834±0.014	2.50±0.24	$1.5\cdot10^{-12}$	<85	σ$_\perp$	This work
KDP pure [a]	$1.2\cdot10^4$	0.803±0.011	2.58±0.18	$6.0\cdot10^{-12}$	<85	σ$_\perp$	This work
KDP pure [a]	0	0.53±0.02	–1.73±0.04	$1.4\cdot10^{-11}$	20–100	σ$_{\|\|}$ [e]	[5]
KDP pure [b]	0	0.99±0.02	4.25±0.15	$1.7\cdot10^{-13}$	100–180	σ$_{\|\|}$	[5]
KDP pure [a]	0	0.540±0.004	–1.17±0.07	$3.5\cdot10^{-11}$	–40–180	σ$_\perp$	[3]
KDP pure [b]	0	0.78±0.07	2.0±0.9	$3.9\cdot10^{-12}$	180–200	σ$_\perp$	[3]
KDP:0.10%SO_4 [a]	0	0.52±0.01	–0.3±0.3	$5.8\cdot10^{-10}$	20–100	σ$_\perp$	[3]
KDP:0.14%SO_4 [a]	0	0.52±0.01	–0.2±0.2	$7.3\cdot10^{-10}$	20–110	σ$_\perp$	[3]
KDP:0.26%SO_4 [a]	0	0.525±0.009	0.2±0.15	$1.5\cdot10^{-9}$	20–110	σ$_\perp$	[3]

[a] Low-temperature parameters of conductivity.
[b] High-temperature parameters of conductivity.
[c] The values of room temperature conductivity (σ$_{RT}$) were calculated using the parameters contained in the table.
[d] σ$_\perp$ – the values of conductivity along the crystallographic *a* axis.
[e] σ$_{||}$ – the values of conductivity along the crystallographic *c* axis.
Results are presents as calculated parameter ± standard error.

of the conductivity caused by heating of the crystal, do not occur.

Shown in Table 2 are the calculated conductivity parameters. The conductivity of the non-irradiated crystal is described by (1) which contains two exponents. Their parameters are presented in the table.

After irradiation of the crystal with gamma-ray doses in $1.2\cdot10^3$-$2.7\cdot10^3$ Gy range corresponding to the minimum conductivity values for the irradiated crystals, the temperature dependence becomes monoexponential (Fig.2). It is described by only one term in (1), the pre-exponential factor and the activation energy within the limits of measurement accuracy are equal to the corresponding parameters of the conductivity of the unrradiated crystal at *T*>85°C (above the kink, Fig. 2). For the crystals irradiated with higher doses $D>2.7\cdot10^3$ Gy in the studied temperature range the temperature dependences are also monoexponential. As seen from Table 2, the parameters of the exponents depend on the irradiation dose.

Chemical analysis. The conductivity of irradiated KDP crystals essentially depends on the presence of aliovalent anionic and cationic impurities [3, 5, 6, 16, 17, 20]. As is known, the incorporation of impurity ions into KDP lattice is accompanied with the formation of proton vacancies necessary for local charge compensation. When the number of proton vacancies increases, the conductivity grows, too. According to [6], the conductivity value is influenced by the cationic impurities Fe, Al. The anionic impurities such as SO_4 with 0.10÷0.26 % concentration in KDP anionic sublattice also increase the conductivity characterized by an activation energy of 0.52÷0.525 eV [3] (Table 2). This activation energy is defined by migration of proton vacancies (*L*-defects). As will be shown below, this value is very close to 0.522 eV obtained in the present study for the low-temperature range *T*<85°C (Table 2). This testifies that the crystals investigated there are characterized by similar conductivity mechanism bound up with migration of proton vacancies. The presence of impurity ions in a sufficient concentration in the studied samples (Table 1) is an additional factor which shows that in the low-temperature range unirradiated KDP crystals possess the impurity conductivity, which mechanism is also related to migration of proton vacancies.

Analysis of dose dependences. The analysis of the dose dependences σ(*D*) (Fig.1) shows that they are characterized by the three components:

Table 3. Parameters of the exponents used in the expression for the dose dependences of conductivity of KDP crystals.

D_{τ} (10^3·Gy)	$\sigma_{exp}(0)$ (10^{-11}·S/cm)	σ_{const} (10^{-13}·S/cm)	Notes
0.51±0.06	1.12±0.05	2.6±0.31	This work
1.40±0.19	3.04±0.15	58.0±0.44	[18]

$$\sigma(D)= \sigma_{exp}(D) + \sigma_{const} + \sigma_{slow}(D), \qquad (2)$$

where $\sigma_{exp}(D)$ is the "exponential" component of the dose dependence;

σ_{const}, the constant (weakly dependent on irradiation dose) conductivity component;

$\sigma_{slow,}$, the conductivity component which increases slowly over the range of irradiation doses $2.7\cdot10^3$-$2\cdot10^4$ Gy.

The conductivity component $\sigma_{exp}(D)$ is dominating at the doses $D<1.2\cdot10^3$ Gy. At such doses, when the contribution of $\sigma_{slow}(D)$ to the total conductivity value is insignificant (Fig. 3), the value of conductivity is described by the following expression:

$$\sigma(D) = \sigma_{\exp}(0)\exp(-D/D_{\tau}) + \sigma_{const} \qquad (3)$$

The parameters $\sigma_{exp}(0)$, D_{τ}, σ_{const} are presented in Table 3. As follows from this table, they considerably differ from the corresponding values earlier reported in [18] for KDP crystals with another impurity composition. Apparently, σ_{exp}, D_{τ}, σ_{const} depend on the crystal growth conditions and the defects present in such crystals.

The value of σ_{const} probably corresponds to the mechanism of intrinsic conductivity related to thermal generation and migration of crystal defects, or/and to the impurity mechanism characterized by high activation energy. The value of σ_{const} equal to $2.6\cdot10^{-13}$ S/cm (Table 2) has the same order of magnitude as $1.7\cdot10^{-13}$ S/cm value that corresponds to the intrinsic mechanism reported in [5] (Table 2). Therefore, it should be assumed that the mechanism of intrinsic conductivity contributes to σ_{const}. Moreover, there may exist the contribution of another mechanism of conductivity to σ_{const} which requires high activation energy E_a~0.8 eV.

High radiation resistance of the crystal lattice [21] and the observed wherein essential change in the conductivity components at the irradiation doses up to $2\cdot10^4$ Gy show that the revealed radiation effects are mainly defined by the processes of disappearance and transformation of the growth defects present in the crystals prior to their irradiation. It is known [6],

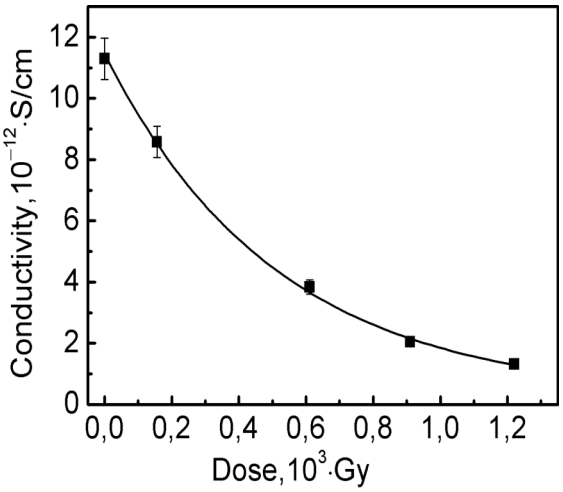

Fig. 3. Exponential dependence of electrical dc c onductivity in KDP single crystal at low gamma-irradiation doses: the experimental points and the exponential fit of the data (solid line).

that local compensation of the charge state of some impurity ions in KDP crystals occurs with participation of the defects that influence the conductivity. The study of defects in KDP with the electron paramagnetic resonance (EPR) spectroscopy [22] shows that the introduction of iron ions into KDP crystal leads to the appearance of two proton vacancies.

As a rule, the processes of formation of radiation defects with participation of impurities are accompanied with a change in the charge state of the impurity ions. In its turn, this influences the quantity of the defects (in particular, proton vacancies) necessary for local compensation of the charge of radiation-modified impurity ions and, consequently, of the quantity of mobile crystal lattice defects responsible for the conductivity.

Therefore, the decrease in the conductivity component $\sigma_{exp}(D)$ in KDP crystals at irradiation with doses $D<2.7\cdot10^3$ (Fig. 1, 3) can be explained by the diminishing concentration of proton vacancies. This may be caused by the following factors:

– changes in the charge state of the anionic or cationic impurity defects, or of another

mechanism of their transformation resulting in a decrease of the concentration of charge-compensating proton vacancies;

– decreasing quantity of proton vacancies due to the interaction of a proton vacancy (*L*-defect) with atomic hydrogen or proton (atomic hydrogen is observed by EPR method at irradiation of the crystals of potassium dihydrophosphate type [18]).

As is known [3], the presence of a certain quantity of SO_4 impurity defects in potassium dihydrophosphate crystal leads to formation of the same quantity of proton vacancies (*L*-defects). The authors of [3] determined the mobility of *L*-defects formed at the incorporation of HSO_4 ions into KDP ($\mu_L = 6 \cdot 10^{-10}$ cm$^2 \cdot$V$^{-1} \cdot$s^{-1}). So, the concentration of *L*-defects can be found using the expression:

$$\sigma_L = N_L \cdot e \cdot \mu_L \qquad (4)$$

where σ_L is the conductivity caused by the presence of *L*-defects,

N_L, the quantity of defects in 1 cm^3,

e, electron charge,

μ_L, mobility of proton vacancy.

The investigated KDP crystals, both undoped and doped with SO_4 [3, 5] (Table 2), have the same activation energies of the impurity conductivity (E_{a01}=0.52 eV). Since the conductivity of the crystals studied in [3, 5] is related to migration of *L*-defects, it should be assumed that the impurity conductivity of the undoped crystals investigated in the present work is also caused by migration of L-defects. This allows to determine their concentration from (3) and (4). The obtained dependences of the concentration of *L*-defects on the dose of gamma-irradiation are presented in Fig.4.

At $2.7 \cdot 10^3$-$2.0 \cdot 10^4$ Gy doses there dominates the conductivity component σ_{slow}, responsible for the growth of $\sigma = \sigma_{exp} + \sigma_{const} + \sigma_{slow}$ within the said range. It is increasing in proportion to the irradiation dose: $\sigma_{slow}(D) = kD$. The conductivity rise at the doses D> $2.7 \cdot 10^3$ Gy testifies to the formation of the defects that participate in the processes of charge transfer. At the said doses the conductivity activation energy E_a~0.8 eV is higher than the activation energy of the process of proton vacancy migration. Herewith, the value of conductivity at room temperature at *D*> $2.7 \cdot 10^3$ Gy irradiation doses considerably exceeds the value of intrinsic conductivity of the crystal. So, it should be assumed that the mechanism of conductivity at $2{,}7 \cdot 10^3$-$2 \cdot 10^4$ Gy doses differs from the two above-considered

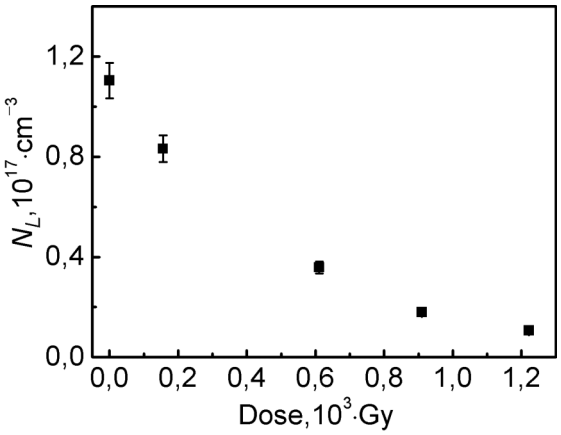

Fig. 4. Changes in the concentration of *L*-defects depending on gamma-irradiation dose in undoped KDP crystals.

conductivity mechanisms responsible for its components σ_{exp} and σ_{const}.

Thus, the presence of "fast", "constant" and "slow" components in the dose dependences of the electrical dc conductivity (Table 3) testifies to the existence of three different conductivity mechanisms.

Analysis of temperature dependences. The obtained results shown in Fig. 2 and Table 2 show that gamma-irradiation have an essential influence on the behaviour of the temperature dependences and the conductivity parameters.

Before irradiation the temperature conductivity dependences of KDP crystals have a kink (Fig. 2). Similar kink was also observed in other works, but at another temperature. In particular, in [5] such a kink was reported to appear at *T*=100 ºC. Its presence in the temperature dependences is explained in [3-6] by the existence of two types of conductivity: impurity and intrinsic – dominating in the low– and high-temperature ranges, respectively. The impurity conductivity is characterized by lower values of the activation energy E_a and of the pre-exponential factor σ_0 in comparison with the intrinsic conductivity: $E_{a01} < E_{a02}$ and $\sigma_{01} < \sigma_{02}$ in Exp. (1). In the present study (Table 2) E_{a01}= 0.522 eV corresponds to the impurity mechanism (migration of proton vacancies), whereas E_{a02}= 0.835 eV testifies to the intrinsic mechanism (formation and migration of proton vacancies).

Low γ-irradiation doses (down to $3 \cdot 10^3$ Gy) mainly affect the impurity conductivity component related to migration of proton vacancies which disappears completely at the irradiation doses *D*>$2.7 \cdot 10^3$ Gy (Fig. 2, Table 2). Thereat, in the low– and high-temperature ranges the

temperature dependences are characterized by the same behaviour. In this case the kink of the temperature dependence observed in the unirradiated crystals at T=85 °C, is absent The residual conductivity that corresponds to the minimum of the dose dependence is bound up with the intrinsic mechanism for which $E_a \geq 0.8$ eV [6]. Moreover, there may also take place the contribution of the impurity mechanisms including those that involve not only migration, but also formation of mobile defects related to overcoming a certain potential barrier.

In $(1.2\text{-}2.7)\cdot10^3$ Gy dose range, when the conductivity at room temperature is minimal, the activation energy essentially rises. As reported in [6], the crystals with a higher activation energy have a higher perfection. High E_a values testify to predominance of the intrinsic, or of some impurity mechanism of conductivity for which the value of electrical ac conductivity can reach 0.7 eV [6]. Such a fact makes it possible to conclude that in some cases low gamma-irradiation doses $D < 2.7\cdot10^3$ Gy allow to improve the characteristics of the crystals.

The increase in the conductivity value at room temperature at the doses exceeding $2.7\cdot10^3$ Gy points out to formation of defects in the crystals, such as protons in the interstices which migration is bound up with the conductivity mechanism. The following facts testify in favour of the conductivity mechanism associated with migration of protons along the interstices:

– the activation energy for the said process may be high enough (E_a~0.7 eV) [6] , that is close to the activation energy E_a ~0,8 eV obtained in the present study for the KDP crystals irradiated with doses exceeding $2.7\cdot10^3$ Gy (Table 3);

– at the same time it is less than the activation energy for the intrinsic conductivity mechanism E_a = 0.99 eV [5], for the ac conductivity $E_a \geq 0.8$ eV) [6].

4. Conclusions

Non-monotonic dose dependence of the conductivity of potassium dihydrophosphate crystals is related to the existence of at least three conductivity mechanisms which dominate in different ranges of gamma-irradiation doses.

The most sensitive to gamma-irradiation is the mechanism bound up with migration of proton vacancies (L-defects) which contribution to the conductivity can be reduced by an order of magnitude at gamma-irradiation.

The least sensitive to gamma-irradiation is the intrinsic mechanism related to thermal generation and migration of proton vacancies.

Gamma-irradiation with the doses exceeding $2.7\cdot10^3$ Gy increases the conductivity related to the mechanism of proton transfer along the interstices.

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