Functional Materials 18, No.2 (2011)

Gamma-ray-induced decrease of *L*-defect concentration in KDP single crystals

A.N.Levchenko, I.M.Pritula*, V.B.Tyutyunnik, A.P.Gavrik, O.T.Nikolov

V.Karazin Kharkiv National University,
4 Svobody Sq., Kharkiv 61022, Ukraine
*Institute for Single Crystals, STC "Institute for Single Crystals",
National Academy of Sciences of Ukraine, 60 Lenin Ave., 61001 Kharkiv,
Ukraine

Received January 9, 2011

The dependence of electrical dc conductivity of KH_2PO_4 (KDP) single crystals on the dose of γ-irradiation is investigated. The conductivity is found to decrease exponentially at γ-irradiation. The temperature dependences of the conductivity are described by the exponential law. The pre-exponential factor and activation energy values of conductivity are determined for the crystals irradiated with various doses. Analysis of the dose and temperature dependences shows that the radiation-induced decrease of the conductivity is associated with the decrease of *L*-defect concentration in the crystal. The concentration changes in accordance with the law of first order kinetics at the range of γ-irradiation doses of $3.0 \cdot 10^2 \div 6.3 \cdot 10^3$ Gy. Possible mechanisms of the *L*-defect concentration changes under γ-irradiation of crystals are discussed.

Исследована зависимость удельной электропроводности монокристаллов KH_2PO_4 от дозы γ-облучения. Установлено, что при γ-облучении происходит экспоненциальное уменьшение электропроводности. Температурные зависимости электропроводности подчиняются экспоненциальному закону. Определены значения предэкспоненциального фактора и энергии активации электропроводности для кристаллов, облучённых различными дозами. Анализ дозовых и температурных зависимостей показывает, что радиационно-индуцированное уменьшение величины электропроводности связано с уменьшением концентрации *L*-дефектов в кристаллах. Изменение концентрации в интервале доз γ-облучения $3.0 \cdot 10^2 \div 6.3 \cdot 10^3$ Гр происходит в соответствии с законом кинетики первого порядка. Обсуждаются возможные механизмы изменения концентрации *L*-дефектов при γ-облучении кристаллов.

1. Introduction

Potassium dihydrogen phosphate (KDP, KH_2PO_4) single crystals have found wide use in laser facilities as elements of electrooptical switches, modulators and deflectors [1]. The crystals used in electrooptical devices must have rather high ohmic resistance, therefore dc electrical conductivity is a significant characteristic of such crystals. Its value depends on the crystal growth and radiation defects [2–5]. The formation of growth microdefects is caused e. g. by incorporation of impurities into the lattice in the process of crystal growth, or by non-stoichiometry (violation of the stoichiometry) of the growth solution. Radiation defects are formed in the crystals under the action of electromagnetic radiation with high quantum energy. Study of the influence of different kinds of radiation on dc electrical conductivity of KDP crystals

is significant both for improvement of their electrophysical characteristics and for investigation of the mechanisms of the formation of radiation defects.

The crystal structure of KH_2PO_4 consists of K^+ cations and $H_2PO_4^-$ anions. The phosphate ions PO_4^{3-} are connected with each other by the hydrogen bonds. At $T > T_c = -150$°C (123 K) the crystals are in paraelectric phase and have the tetragonal symmetry $I\bar{4}2d$ [6]. The conductivity σ in KDP crystals is defined by migration of the protons H^+ and the proton vacancies V_{H+} (L-defects) [2–4], and is described by the equation:

$$\sigma = \sigma_0 \cdot \exp(-\frac{E_0}{kT}), \quad (1)$$

where σ_0 is the preexponential factor, E_a, the activation energy of conductivity, k, the Boltzmann constant, T, the absolute temperature. If there are some conduction mechanisms, the right-hand side of Eq.(1) may contain several terms with σ_0 and E_a values corresponding to each mechanism.

As reported in [5], under irradiation of the crystals with ionizing radiation the value of dc conductivity changes. However, the mechanism of the influence of irradiation on the conductivity can be established on the base of a detailed study of the dose and temperature dependences, as well as irradiation-induced changes in the concentration of the defects which influence the conductivity.

The goal of the present work was to investigate the γ-induced changes in the concentration of the defects responsible for dc conductivity in potassium dihydrogen phosphate crystals, and to determine the effect of irradiation on the values of σ_0 and E_a.

The investigated crystal samples were grown by the method of solvent re-circulation at a rate of 1–3 mm/day. The impurity composition of the samples was established by the standard methods of atom-emission spectrometry (see Table 1). The amount of ^{75}As impurity in potassium dihydrogen phosphate solutions determined in accordance with [12] was 10^{-4}–10^{-3} wt.%.

The radioactive isotope ^{60}Co was used as a source of γ-rays; the irradiation doses varied within $2.8 \cdot 10^2$–10^7 Gy range.

2. Experimental

For the investigated unirradiated and irradiated KDP samples, the difference in the values of dc conductivity measured along the axis c and perpendicular to it, did not exceed 20–35 % (100 % $\cdot|\sigma_\parallel - \sigma_\perp|\sigma_\parallel \sim 20 \div 35$ %). In this paper we present the results of the measurements of the axial conductivity component.

Table 1. Results of impurity composition analysis for KDP crystals

Impurity content (wt.%)				
Pb	Si	Fe	Al	Ca
$<5 \cdot 10^{-5}$	$2.7 \cdot 10^{-3}$	$1.8 \cdot 10^{-4}$	$2 \cdot 10^{-3}$	$2.8 \cdot 10^{-3}$

The value of dc conductivity was measured for the electric field intensities E = 152–556 V/cm. In this range the voltage-current characteristic of the crystal is linear enough [8], so it is possible to compare the results of dc conductivity measurements obtained at different applied voltage and different sample's thickness of the sample.

To obtain the data concerning the conduction mechanism, we investigated the temperature dependences of the conductivity and determined the values of σ_0 and E_a from these dependences using the method of least squares. The said dependences were measured by "E6-13A" teraohmmeter (the instrumental error being ±4 %) at E = 152–556 V/cm. The measurements were carried out within 20–146°C interval. To obtain the required temperature of the crystal samples, a 2B-151 type thermostat with an electric heater unit was used. The temperature was measured by a differential copper-constantan thermocouple. One (cold) end of the thermocouple was placed in a thermostat with a temperature of 0°C, the other end was in contact with the investigated sample. The conductivity measurements were carried out using the conventional two-probe technique on the crystal samples shaped as parallelepipeds with two opposite faces covered with graphite to provide good ohmic contacts with the crystal investigated. The resistance of the samples was measured at a voltage of 100 V. The conductivity of the crystals was found from the relation:

$$\sigma = \frac{t}{R \cdot S}, \quad (2)$$

where R is the resistance of the sample, t, the thickness of the sample, S, the area of the crystal sample faces covered with graphite, $S = A \times B$, with A and B being the dimensions of the sample.

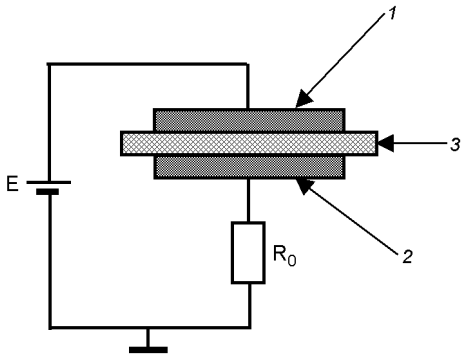

Fig. 1. Two-electrode circuit for measurement of dc conductivity of the crystals: E — power supply; R_0 — measuring resistor; *1*, *2* — electrodes; *3* — crystal sample.

The dependence of dc conductivity on the dose of γ-irradiation (the dose dependence) was measured along the *c*-axis at the electric field intensity equal to 218 V/cm by means of the circuit shown in Fig. 1, using current-conducting rubber electrodes. The power supply voltage was $\mathcal{E} = 50$ B, the value of the standard resistor was $R_0 = 10^8$ Ohm. The voltage across the standard resistor was measured by a direct current electrometric voltmeter VK2-16. The voltmeter error and the uncertainty of the current value in the measurements using potential drop across the standard resistor were ±1.5 % and ±10 %, respectively. A constant-voltage power supply TES20 was used as a voltage supply. The measurements were carried out at the temperature T = 25±0.5°C. The mentioned instability of the crystal sample temperature leads to inaccuracy of the resistance measurements of 3.5 ÷ 4.8 % at E_a = 0.52 ÷ 0.72 eV.

The resistance of the sample R was determined from the formula:

$$R = R_0[(\mathcal{E}/U) - 1], \qquad (3)$$

where $\mathcal{E}$ is the power supply voltage, R_0, the resistance of the standard resistor, U, the voltage drop across the standard resistor.

The conductivity of the crystals was found from relation (2) in which S is the area of the crystal faces contacting with the electrodes.

While measuring dose dependences, the standard error of dc conductivity measurements, taking into account the uncertainty of the crystal temperature, the dimensions of the crystal sample and the instrumental error did not exceed 11 %.

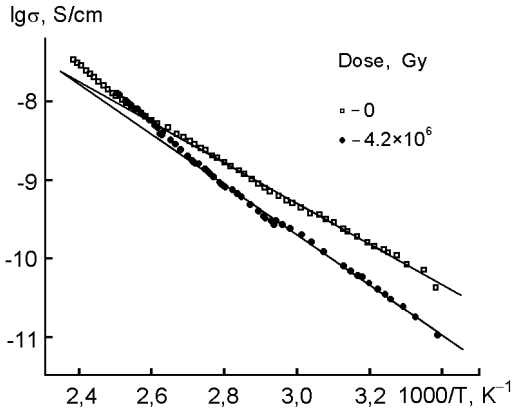

Fig. 2. Temperature dependences of electrical dc conductivity of non-irradiated and γ-irradiated KDP crystals (the solid lines denote lgσ values calculated based on the parameters from Table 2).

The samples used in this study had the following dimensions: A = 1.0 ÷ 1.2, B = 1.0 ÷ 1.5, t = 0.18 ÷ 0.66 cm.

3. Results and duscussion

In a number of cases the dc conductivity parameters σ_0 and E_a determined by analyzing the temperature dependences give the information concerning the mechanism of charge transfer. As shown in [3], for KDP crystals the value $E_{a1} \approx 0.52$–0.55 eV points to the processes of the migration of proton vacancies (*L*-defects), whereas $E_{a2} > E_{a1}$, $E_{a2} \approx 0.78$–1.00 eV is usually connected with the process of the formation and migration of intrinsic defects in the crystal [2–4]. At the same time, in non-stoichiometric KDP crystals high E_a values may be also caused by the migration of excessive protons over the interstitials [4]. In the opinion of the authors of the mentioned paper, the crystals with high activation energies are more perfect, since high E_a value testifies to domination of the intrinsic conduction mechanism characterized by $E_a > 0.7$ eV.

The temperature dependences of dc conductivity of the irradiated crystals obtained in the present paper (Fig. 2) have the form of straight line in the Arrhenius coordinates ($1/T$, $\lg\sigma_0$) in the temperature range of 20 ÷ 100°C. This points to the fact that the temperature-dependent changes in dc conductivity of the crystals occur in accordance with Eq.(1).

The values σ_0 and E_a are calculated from the slope of the conductivity curve towards the axis X and the intercept of this curve

Table 2. Electrical dc conductivity parameters for KDP single crystals*

Sample number	Dose (Gy)	E_a (eV)	$\lg\sigma_0$ (S/cm)	σ_{RT} [c] (S/cm)	σ_{25} [c] (S/cm)	T(°C)
1[a]	0	0.520±0.005	−1.51±0.08	$3.6\cdot10^{-11}$	$5.0\cdot10^{-11}$	<130
1[b]	0	0.796±0.009	2.1±0.1	$2.6\cdot10^{-12}$	$4.4\cdot10^{-12}$	130–145
2[a]	$2.8\cdot10^4$	0.570±0.009	−1.20±0.11	$1.0\cdot10^{-11}$	$1.5\cdot10^{-11}$	<100
3[a]	$4.2\cdot10^6$	0.636±0.005	−0.07±0.07	$9.9\cdot10^{-12}$	$1.5\cdot10^{-11}$	<100
3[a,d]	$4.2\cdot10^6$	0.540±0.006	−1.26±0.08	$2.9\cdot10^{-11}$	$4.1\cdot10^{-11}$	<100
4[a]	10^7	0.720±0.011	1.45±0.10	$1.2\cdot10^{-11}$	$1.9\cdot10^{-11}$	<100

* The results are presented as the calculated parameters ±standard error. The main results were obtained at increasing the temperature of the crystals irradiated 10 (sample 2) and more than 15 years (samples 3, 4) before; E_a and σ_0 values were calculated without weighting;
[a, b] low-temperature ($T < 130$°C) and high-temperature ($T > 130$°C) conductivity parameters, respectively;
[c] the values conductivity at room temperature (σ_{RT}) and at 25°C were calculated using the parameters contained in the Ttable;
[d] low-temperature parameters of conductivity were determined at cooling of the crystal from 145°C down to room temperature.

on the axis Y. The calculated parameters of the dc conductivity of potassium dihydrogen phosphate crystals are presented in Table 2.

As follows from the Table, the conductivity parameters of the irradiated crystals vary within rather wide interval: $E_a = 0.52 \div 0.72$ eV, $\lg\sigma_0 = -1.51 \div 1.45$ S/cm.

Analysis of the results obtained in the present study show that for KDP-type crystals the value of dc conductivity is defined by the expression [2]:

$$\sigma = \sigma_{01} \cdot \exp(-\frac{E_{a1}}{kT}) + \sigma_{02} \cdot \exp(-\frac{E_{a2}}{kT}), \quad (4)$$

where σ_{01}, σ_{02} are the preexponential factors, E_{a1}, E_{a2}, the activation energies corresponding to different mechanisms of dc conduction. The first term in Eq.(4) is the structure-dependent component of the conductivity (defined by the lattice imperfections and connected with the migration of L-defects). The second term describes the conductivity caused the processes of formation and migration of the intrinsic and, probably, some types of impurity defects.

For the unirradiated potassium dihydrogen phosphate crystals studied in the present work $E_{a1} \approx 0.52$ eV. This testifies that in the vicinity of room temperature the mechanism of dc conduction caused the migration of L-defects is dominating. In the crystals irradiated with high doses ($D = 10^7$ Gy) $E_{a2} = 0.72$ eV. In this case the intrinsic conduction mechanism and the

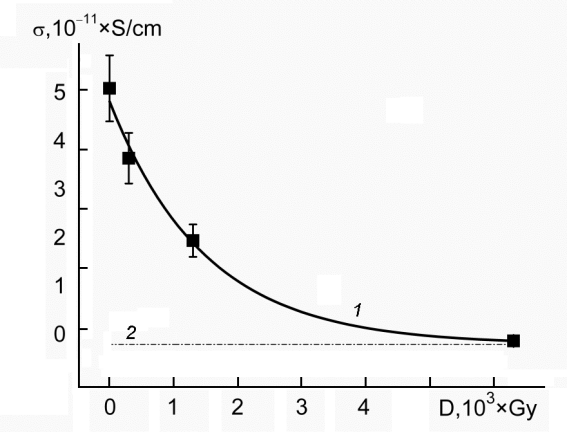

Fig. 3. Electrical dc conductivity of KDP single crystals versus γ-irradiation dose (*1*) and dose-independent component of conductivity $\sigma_2 \approx$ const (*2*). The conductivity was measured along *c*-axis at 25°C (the solid lines denote lgσ values calculated from formula (5)).

mechanism caused the proton migration over the interstitials, may be realized.

Fig. 3 shows the dependence of the dc conductivity of KDP single crystals $\sigma_{\|}$ measured along the crystal axis *c* on the dose of γ-irradiation. One can see that even at comparatively low doses ($D \le 6.3\cdot10^3$ Gy) the conductivity value essentially changes. After γ-irradiation with $D > 3\cdot10^4$ Gy the room temperature conductivity diminishes by an order.

The observed essential change of the conductivity occurs in the vicinity of room temperature where the values σ_0 and E_a are

sensitive to defects formed in crystals, as well as in the range of γ-irradiation doses where KDP crystal lattice is radiation-resistant [9]. This allows to assume that the observed effects are mainly defined by modification of the structure of the growth defects present in the crystal.

As seen from Fig. 3, there are two conductivity components σ_1 an σ_2, one of them essentially depends on the irradiation dose. The dose dependences of dc conductivity may be presented as:

$$\sigma(D) = \sigma_1(D) + \sigma_2 = \sigma_{10} \cdot \cdot \exp\left(\frac{D}{D_0}\right) + \sigma_2, \quad (5)$$

where σ_1 and $\sigma_2 \approx$ const are the two conductivity components with low ($E_a \sim 0.5$ eV) and high ($E_a > 0.7$ eV) value of activation energy, respectively; σ_{10}, the constant factor corresponding to the value of the dc conductivity σ_1 of the unirradiated crystal, D, the dose of γ-irradiation, D_0, the constant value measured in Gy and numerically equal to the dose of γ-irradiation at which the conductivity component σ_1 diminishes by e times. For the investigated crystal $\sigma_{10} = (4.1 \pm 0.4) \cdot 10^{-11}$ S/cm, $\sigma_{20} = (0.73 \pm 0.12) \cdot 10^{-11}$ S/cm, $D_0 = (1.5 \pm 0.4) \cdot 10^3$ Gy.

The γ-induced decrease of the dc conductivity of KDP single crystals observed after γ-irradiation is stable enough. Heating of the irradiated sample up to 100°C did not increase the conductivity value. The conductivity of the samples irradiated with $D \approx 3 \cdot 10^4$ Gy remained by $3 \div 3.6$ times lower in comparison with the one of the unirradiated samples at storage of the irradiated crystals during $10 \div 15$ years at 25±5°C (Table 2).

It is known that the doses of γ-irradiation $D \sim 10^4$ Gy lead to transformation of the defects [10], but do not have essential influence on KDP crystal structure perfection [9]. So, γ-irradiation can be used for decreasing the dc conductivity of the crystals.

However, heating of the crystals up to temperatures higher than 130°C essentially increased their dc conductivity (Fig. 2). As seen from the figure, at highest temperatures the value of dc conductivity of the irradiated crystals became close to that of the unirradiated crystals. In this case there occured irreversible changes in the conductivity parameters: E_a and $\lg\sigma_0$ diminish,

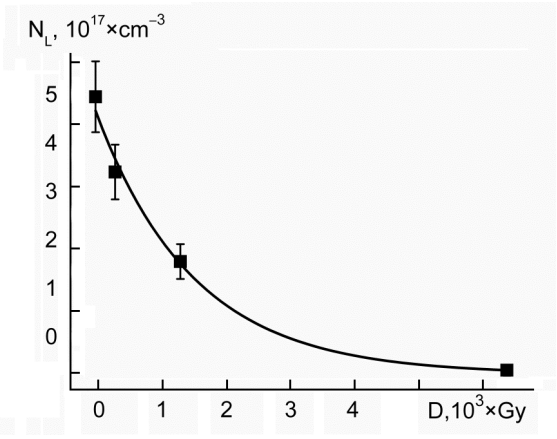

Fig. 4. Dependence of L-defect concentration in KDP crystals on γ-irradiation dose (the solid lines denote lgσ values calculated from formula (7)).

whereas the dc conductivity at room temperature increases (Table 2).

The concentration of L-defects in KDP crystals can be estimated using the results [2], which show that this concentration varies in proportion to the concentration of the introduced HSO_4^- impurity ions. This is connected with the fact that one sulfate ion HSO_4^- which substitutes the phosphate ion $H_2PO_4^-$ produces one protonic vacancy (L-defect) in KDP-type crystals. Therefore, the mobility of L-defects can be determined from the known concentration of the sulfate ions introduced in the crystal:

$$\sigma_L = N_L \cdot q \cdot \mu_L, \quad (6)$$

where σ_L is the conductivity caused by the presence of L-defects, N_L, the quantity of the defects per cm^3, q, the value of the charge of a proton, μ_L, the mobility of L-defects.

Using the known value of protonic vacancy mobility and Eq.(6) one can find the concentration of L-defects in the crystals. At 25°C the mobility of L-defects $\mu_L = 6 \cdot 10^{-10}$ $cm^2 \cdot V^{-1} \cdot s^{-1}$ [2].

For the studied unirradiated crystals with $\sigma_1(0) > \sigma_2$ the activation energy $E_a = 0.52$ eV. This points to the fact that the conductivity $\sigma_1(D)$ in expression (5) is connected with the migration of L-defects. Therefore, the dependence of the concentration of L-defects on the dose of γ-irradiation $N_L(D)$ taking into account $\sigma_{1\parallel} \approx \sigma_{2\perp}$ may be written as:

$$N_L(D) = N_{L0} \cdot \exp(-\frac{D}{D_0}), \quad (7)$$

where N_{L0} is the concentration of L-defects in the unirradiated crystals, D, the dose of γ-irradiation, D_0, the constant value numerically equal to the dose of γ-irradiation at which $N_L(D)$ diminishes by e times. For the investigated $N_{L0} = (4.2\ 0.4)\cdot10^{17}$ cm^{-3}, $D_0 = (1.5\pm0.3)\cdot10^3$ Gy. The dependence of concentration of L-defects on γ-irradiation dose $N_L(D)$ is presented in Fig. 4.

The concentration of L-defects N_{L0} may be also determined as follows [11]:

$$\rho_0 = \frac{h}{q^2 \cdot \delta^2} \cdot N_{L0}^{-1}, \qquad (8)$$

where $\rho_0 = 1/\sigma_0$, σ_0, the preexponential factor in Eq.(1), h, the Planck's constant, q, the charge value, δ, the distance between two steady positions of charge carrier, $\delta \approx 4.6\cdot10^{-8}$ cm [11].

The concentration $N = 3.8\cdot10^{17}$ cm^{-3} in the unirradiated crystals determined from relation (8) ($\lg\sigma_0 = -1.51$ S/cm; $\sigma_{10} >> \sigma_2$) is in rather good agreement with the concentration N_{L0} obtained from relation (6).

As follows from (7), the dependence of the concentration on the dose of γ-irradiation $N_L(D)$ is monoexponential which corresponds to the first-order kinetics law. This is explained by the fact that one of the components participating in the radiation-chemical reaction is present in excess, i.e. its concentration is higher than N_{L0}.

Ionizing irradiation of KDP crystals gives rise to high concentrations of secondary electrons e^-, H^0 atoms (~10^{18} cm^{-3}) as well as $[H_2PO_4]^0$ and $[HPO_4]^-$ radicals (~10^{18} cm^{-3} [12]. The authors of ref. [13] suppose that the formation of the radical $[HPO_4]$ is accompanied with hydrogen bond breakdown. Thereat, the capture of proton H^+ results in the formation of D-defect which influences the value of dc conductivity.

As is known [14], γ-irradiation leads to the following two processes:

$$[H_2PO_4]^- \rightarrow [H_2PO_4]^0 + e^-, \qquad (9)$$

$$[H_2PO_4]^- \rightarrow [HPO_4]^- + H^0. \qquad (10)$$

In the pure KDP crystals, free electron e^-, the atom H^0 and the radicals $[H_2PO_4]^0$, $[HPO_4]^-$ are unstable at room temperature. However, in the presence of impurity ions they may participate in the formation of stable radiation defects.

Below we consider possible radiation-chemical processes which diminish the concentration of L-defects and, consequently, dc conductivity of the crystals.

As mentioned earlier, chemical analysis testifies to the presence of Fe, Al, Cr, As and other impurities in the investigated crystals. The ions of the said impurities enter into the structure of KDP-type crystals substituting the ions K^+ and P^{5+} [15, 16]. Thereat, protonic vacancies are formed. For instance, if in the process of crystal growth the ions Fe^{3+} and Cr^{3+} occupy the K^+ position, there are formed two protonic vacancies V_{H+} which are necessary for local compensation of the impurity ion charge. If the ions As^{5+} enter into the P^{5+} position, protonic vacancies near arsenic ions are not formed.

Under γ-irradiation of the crystals the growth defects undergo transformations [10, 15] accompanied with changes in their charge state. In particular, due to electron capture the arsenate ion AsO_4^{3-} which isomorphically substitutes the phosphate ion PO_4^{3-} in the crystal lattice of KDP, transforms into the paramagnetic center AsO_4^{4-} as a result of electron capture, whereas the ion Cr^{6+} transforms into Cr^{5+}.

The protonic vacancy V_{H+} (L-defect) which compensates the excessive electric charge +1 of the impurity ion in the anionic sublattice of the crystal may disappear in the process of γ-irradiation at the interaction of the defect with the atom of hydrogen:

$$[XO_4^{2-}V_{H+}]^{2-} + H^0 \rightarrow [XO_4^{3-}H^+]^{2-}, \qquad (11)$$

or at successive electron and proton capture:

$$[XO_4^{2-}V_{H+}]^{2-} + e^- \rightarrow [XO_4^{3-}V_{H+}]^{3-}, \qquad (12)$$

$$[XO_4^{3-}V_{H+}]^{3-} + H^+ \rightarrow [XO_4^{3-}H^+]^{2-}, \qquad (13)$$

where H^0 is hydrogen atom, $[XO_4{}^{2-}V_{D+}]^{2-}$, the impurity molecular ion, e.g. FeO_4^{2-}, SO_4^{2-} [2], CrO_4^{2-} [5] associated with the protonic vacancy V_{H+}, which substitutes the phosphate ion PO_4^{3-} in KDP crystal lattice. The assumption concerning the existence of a protonic vacancy near CrO_4^{2-} follows from Ref. [17] where it is reported that the introduction of the molecular ion in the crystal lattice of KDP increases its conductivity.

If the protonic vacancies compensate the excessive charge of the trivalent impurity metal ion Me^{3+} in the cationic position K^+,

the following processes can explain the change of their concentration:

$$[V_{H+}Me^{3+}V_{H+}]^{+} + H^{0} \rightarrow [V_{H+}Me^{2+}H^{+}]^{+}, \quad (14)$$

or:

$$[V_{H+}Me^{3+}V_{H+}]^{3+} + e^{-} \rightarrow [V_{H+}Me^{2+}V_{H+}]^{2+}, \quad (15)$$

$$[V_{H+}Me^{2+}V_{H+}]^{2+} + H^{+} \rightarrow [V_{H+}Me^{2+}H^{+}]^{3+}, \quad (16)$$

where $[V_{H+}Me^{3+}V_{H+}]^{3+}$ is the crystal structure defect consisting of an impurity ion Me (Me = Fe^{3+}, Cr^{3+}) with the charge +3 located in the position of the crystal lattice cation K^{+}, and two protonic vacancies V^{H+} which compensate its excessive (+2) positive charge.

Some radiation defects formed by electron capture or loss in the process of irradiation (e.g. the radical AsO_4^{4-}) are stabilized at room temperature without local charge compensation. The processes of their formation may also influence the conductivity because the capture or loss of an electron by an impurity ion changes the charge state of other ions of the crystal.

The radiation paramagnetic center HPO_4^{-} in (10) is unstable at room temperature. Therefore, the change in the conductivity observed in the present study cannot be connected with this center. However, in the presence of impurities its disappearance may be bound up with the formation of radiation defects stable at room temperature [18], which may influence the dc conductivity of the crystal.

4. Conclusions

The temperature dependences of the dc conductivity of γ-irradiated potassium dihydrogen phosphate crystals are exponential. At $3.0 \cdot 10^2 \div 1.0 \cdot 10^7$ Gy irradiation doses the activation energy of dc conductivity activation rises from $E_a = 0.52$ eV to $E_a > 0.72$ eV, the logarithm of preexponential factor increases from $\lg\sigma_0 = -1.51$ to $\lg\sigma_0 > 1.45$.

As a result of the irradiation, the change of dominating mechanism of dc conductivity occurs. In the unirradiated crystals and in those irradiated with low doses (up to $3.0 \cdot 10^3$ Gy) the extrinsic mechanism connected with migration of protonic vacancies, is dominating. At high doses there may be realized the intrinsic mechanism which includes thermally activated processes of the formation and migration of crystal defects, as well as the mechanism connected with the migration of protons over the interstitials.

Irradiation of KDP crystals with γ-rays leads to exponential decrease of their dc conductivity. It is established that the radiation-induced change of the concentration of *L*-defects corresponds to the law of first-order kinetics. Proposed are possible mechanisms explaining the change of the concentration of *L*-defects and the conductivity of the crystals.

The changes in the conductivity induced by γ-irradiation are stable in time. In this connection the treatment of the crystals with γ-radiation can be used for raising their ohmic resistivity.

References

1. V.M.Puzikov, V.I.Salo, M.I.Kolybayeva et al., Single Crystals of KDP/DKDP for Power Lasers. Growth, Properties, Applications, Institute for Single Crystals, Kharkiv (2004) [in Russian].
2. M.O'Keeffe, C.T.Perrino, *J. Phys. Chem. Solids*, **28**, 211 (1967).
3. L.B.Harris, G.J.Vella, *J. Chem. Phys.*, **58**, 4550 (1973).
4. E.D.Yakushkin, E.P.Efremova, A.I.Baranov, *Crystallography Rep.*, **46**, 30 (2001).
5. A.N.Levchenko, A.P.Gavrik, I.M.Pritula et al., in: Proc. of LFNM'2006, Kharkiv, Ukraine (2006), p.254.
6. F.Jona, G.Shirane, Ferroelectric Crystals, Pergamon Press, New York (1962).
7. L.D.Alfimova, Yu.N.Velikhov, O.V.Demirskaya, *Vysokochistye Veshchestva*, No.5, 153 (1991).
8. S.C.Sabharwal, B.Ghosh, R.Y.Deshpande, *Rad. Effects and Defects in Solids*, **30**, 123 (1976).
9. E.V.Peshikov, Radiation Defects in Ferroelectrics, FAN, Tashkent, Abstracts Book, 138 (1986).
10. V.M.Shulga, A.N.Levchenko, *Ukr. Fiz. Zh.*, **37**, 1067 (1992).
11. F.M.Alemaikin, G.I.Il'ina, Yu.M.Polozov et al., in: Electronic Properties of Solids States, Mordvinian State University, Saransk, (1978), p.11.
12. S.D.Setzler, K.T.Stevens, L.E.Halliburton et al., *Phys. Rev.*, **57**, 2643 (1998).
13. E.Diegues, J.M.Cabrera, F.Agullo Lopez, *J. Chem. Phys.*, **81**, 3369 (1984).
14. I.A.McMillan, J.M.Clemens, *J. Chem. Phys.*, **68**, 3627 (1978).
15. K.A.Muller, *Ferroelectrics*, **72**, 273 (1987).
16. N.Y.Garses, K.T.Stevens, L.E.Halliburton et al., *J. Cryst. Growth*, **225**, 435 (2001).
17. B.V.R.Chowdari, R.Y.Sekhar, *Phys. Stat. Sol.(a)*, **54**, 413 (1979).
18. N.S.Dalal, J.N.Herak, C.A.McDowell, *Chem. Phys. Lett.*, **40**, 5 (1976).

Індуковане гамма-випромінюванням зменшення концентрації *L*-дефектів у кристалах KDP

О.М.Левченко, І.М.Притула, В.Б.Тютюнник, О.П.Гаврик, О.Т.Ніколов

Досліджено залежність питомої електропровідності монокристалів KH_2PO_4 (KDP) від дози γ-опромінення. Встановлено, що при опроміненні відбувається експоненційне зменшення електропровідності. Температурні залежності електропровідності підпорядковуються експоненційному закону. Визначено значення експоненційного фактора і енергії активації електропровідності для кристалів, які опромінено різними дозами. Аналіз дозових і температурних залежностей показує, що радіаційно-індуковане зменшення величини електропровідності пов'язано зі зменшенням концентрації *L*-дефектів у кристалах. Змінення концентрації в інтервалі доз γ-опромінення $3.0 \cdot 10^2 \div 6.3 \cdot 10^3$ Гр відбувається відповідно до закону кінетики першого порядку. Обговорюються можливі механізми змінення концентрації *L*-дефектів при γ-опроміненні кристалів.