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The peculiarity of electric conductance of KDP single crystals

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The electrical conductivity of KDP crystals grown by the solvent recirculation and temperature lowering methods has been investigated in the 20–150°C temperature range. The temperature dependences follow an exponential law. The pre-exponential factor and activation energy have been determined. A correlation between pre-exponential factor and the conductance activation energy has been found to exist in undoped crystals within the temperature interval of 20–100°C and the activation energy range of 0.49–0.79 eV. The correlation coefficient is 0.98. This testifies that electrical conduction mechanisms are similar in crystals with low concentration of defects. The results obtained are discussed within the frame of known electrical conduction mechanisms in KDP based on the proton transport.

В интервале температур 20–150°С исследована электропроводность кристаллов KDP, выращенных методом рециркуляции и методом снижения температуры. Температурные зависимости электропроводности подчиняются экспоненциальному закону. Определены предэкспоненциальный множитель и энергия активации электропроводности. Установлено, что в нелегированных кристаллах в температурном интервале 20–100°С и диапазоне энергий активации электропроводности 0,49–0,79 эВ имеется корреляция между значением логарифма предэкспоненциального множителя и энергией активации электропроводности. Коэффициент корреляции составляет 0,98. Это свидетельствует о том, что механизмы электропроводности в кристаллах с низкой концентрацией дефектов являются аналогичными. Полученные результаты обсуждаются в рамках известных моделей механизмов электропроводности в KDP, в основе которых лежит транспорт протона.

The electric conductance is a functional characteristic of importance in potassium dihydrophosphate (KH_2PO_4, KDP) crystals used widely in the quantum electronics [1, 2]. The data on the crystal conductance are necessary to control the functional properties thereof. In this connection, the study of the KDP crystal electric conductance is an actual task. In most works [3–8], the KDP conductance was studied in the paraelectrical phase at $T>T_c = 123$ K. In that phase, the KDP crystals have a tetragonal structure consisting of two interpenetrating lattices formed by PO_4^{3-} tetrahedra and two potassium sublattices K^+. Each PO_4^{3-} group is connected with four neighboring PO_4^{3-} tetrahedra by 2.48 Å long hydrogen bonds [9].

It is just the proton transport that underlies most of the known KDP conduction models. The proton migration processes in the KDP group crystals is confirmed by

coulometric experiments and NMR results [10–14]. The intrinsic conduction mechanisms are based on thermally activated processes of the proton defect formation and migration, while the extrinsic mechanisms are connected with the migration of proton defects existing in the crystal. The proton defects include the D- and L-defects (doubly occupied hydrogen bond and proton vacancy, respectively) and the excess protons in interstices [3–8, 15–18]. The main factors affecting the conduction are anionic and cationic impurities, pH of the initial solution, and sectorial crystal structure.

The electric conductance in KDP crystals is described by the expressions (1) [5, 6] or (2) [3–5]:

$$\sigma = (A/T) \cdot \exp(-E_a/kT), \quad (1)$$

$$\sigma = \sigma_0 \cdot \exp(-E_a/kT), \quad (2)$$

where σ is the conductivity; A, σ_0, the pre-exponential factor; T, absolute temperature; k, Boltzmann constant; E_a the conduction activation energy. The pre-exponential factor A depends on the concentration of mobile defects, the crystal structure and the conduction mechanism. The activation energy E_a depends on the crystal structure and the conduction mechanism. In KDP crystals, the activation energy varies within a wide range of 0.216 to 1.0 eV [6, 7, 16, 17]. The activation energy $E_a \approx 0.5$ eV is related to the L-defect migration [5]. This is confirmed by the fact that this activation energy value $E_a = 0.52–0.53$ eV [3] is typical of the crystals containing the L-defects arising due to doping of HSO_4^- anions into the crystal lattice. The activation energy E_a of 0.8 to 1.0 eV is ascribed usually to the intrinsic conduction mechanism including the formation and migration of proton defects.

The KDP electric conductance with the activation energy $E_a < 0.5$ eV and $0.55 < E_a < 0.8$ eV is studied insufficiently. In [6], the 0.5 to 0.7 eV region of activation energy values at low frequencies is believed to be related to the transition from the extrinsic conduction mechanism to the intrinsic one, while $E_a < 0.5$ eV, to the macroscale defects in the crystals.

It has been shown [6] that according to the existing disordering models in crystals, there is a correlation between the conduction parameters. Within the frame of the selected conduction model, the quantity $\ln\sigma_0$ should be in proportion to the activation energy: $\ln A \sim \ln\sigma_0$. However, no expression for that interrelation is presented in the work mentioned.

The aim of this work is to determine the conduction parameters E_a and $\lg\sigma_0$ for KDP crystals and the correlation there between as well as to estimate the crystal quality basing on those parameters.

The studies were carried out using three nominally pure KDP single crystals grown at STC "Institute for Single Crystals", NAS of Ukraine; in this work, the crystals are designated as C1, C2, and C3. According to the preliminary measurements, the electric conductance of those crystals and its variations due to external factors differ considerably.

The crystals C1 and C2 were grown by the solvent recirculation technique [19] at the growth rate 0.5–1 mm/day; the crystal C3, by the temperature lowering technique [20] at the growth rate 5 mm/day.

The crystals under study have shown a high transmission (about 90 %) essentially within the whole 200–1100 nm spectral region except of a weak absorption band in the 220–230 nm range, thus evidencing a high optical quality of the samples. The Pb, Si, Fe, Al, Ca impurity content was $2\cdot10^{-4}$, $3\cdot10^{-3}$, 10^{-4}, $2\cdot10^{-3}$, $2\cdot10^{-3}$ wt. %.; $5\cdot10^{-5}$, $2.7\cdot10^{-3}$, $1.8\cdot10^{-4}$, $2\cdot10^{-3}$, $2.8\cdot10^{-3}$ wt. %; and 10^{-4}, $9\cdot10^{-4}$, $9\cdot10^{-5}$, 10^{-3}, $4.6\cdot10^{-3}$ wt. %, respectively. In the crystal C3 grown using the high-rate technique, the concentration of Si, Fe and Al as well as the total impurity content was lower than in C1 and C2.

Studied were mainly the plates of z-cut crystals from the growth sector {101} of $1.0\times1.0\times(0.2$ to $0.3)$ cm^3 size. To measure the electric conductance, high purity graphite electrodes were applied on the sample surface. The conductance was measured using a E6-13A teraohmmeter at 100 V electrode voltage, the measurement error being 4 to 6 %. Most measurements were carried out using the two-electrode scheme. In some cases, three-electrode scheme was used providing an enhanced measurement accuracy by the surface current bridging. In this case, the calculations of conduction was corrected for the changed electrode shape.

To determine the conduction parameters E_a and $\lg\sigma_0$, the temperature dependences of conductance were measured. The measurements were made under the crystal heating from room temperature up to 150°C.

The parameters E_a and $\lg\sigma_0$ were determined according to Eq.(2) using the least square method. The expression (2) provides a lower accuracy as compared to (1) due to approximation $A/T \cong \sigma_0$ that causes an error in the calculated values of the actiovation energy (about 5 %) [5]; nevertheless, the use of that expression makes it possible to compare the results of this work with the data obtained by other workers. The same approximation $A/T \cong \sigma_0$ was used when determining the interrelation between the conduction parameters.

Several typical temperature dependences of conduction for the studied KDP samples are shown in Fig. 1. Those are seen to follow the exponential law (1) and to contain some features characteristic for each of the crystals. The conduction-temperature plots for crystals C1 (Fig. 1a) and C2 (Fig. 1b) contain a knee near $T \approx 85$°C and $T \approx 130$°C, respectively. Those are described by two expressions of the (2) type with different conduction parameter values (see Table) for different temperature ranges. The dependences observed for C1 and C2 can be explained by the existence of the extrinsic and intrinsic conduction mechanisms dominating in the low-temperature region and the high-temperature one within the studied temperature range [3–6]. The extrinsic electric conductance is characterized by lower E_a and σ_0 values (the low-temperature conduction parameters) as compared to the intrinsic one (the low-temperature conduction parameters). As to the crystal C3 (Fig. 1c), its temperature dependence of conduction is described by Eq.(2), too, but without any knee within the studied temperature range (20–150°C). At room temperature, the minimum conductance was observed for the crystal C3 having the minimum total impurity content as well as the lowest concentration of Al and Fe. The conductivity of C1 and C2 crystals at room temperature amounts $1.4 \cdot 10^{-11}$ and $3.6 \cdot 10^{-11}$ S/cm, respectively, while for samples made from C3, it is $(0.4–1.3) \cdot 10^{-11}$ S/cm (Table).

The conduction activation energy value ($E_a = 0.52$ eV) near room temperature shows that in C1 and C2, one and the same conduction mechanism dominates connected with L-defect migration [3, 5]. The difference in C1 and C2 conduction at room temperature is connected with different concentrations of L-defects arising in the crystals due to inclusion of aliovalent impurities. The lower conduction of C3 crystal at room temperature as compared to C1 and C2 is connected with higher activation energy in C3 ($E_a > 0.7$ eV), thus evidencing the difference in defect concentrations in the crystals. In contrast to the C1 and C2 conduction, that of C3 is characterized by the absence of any appreciable contribution from the extrinsic component associated with the L-defect migration ($E_a \sim 0.5$ eV).

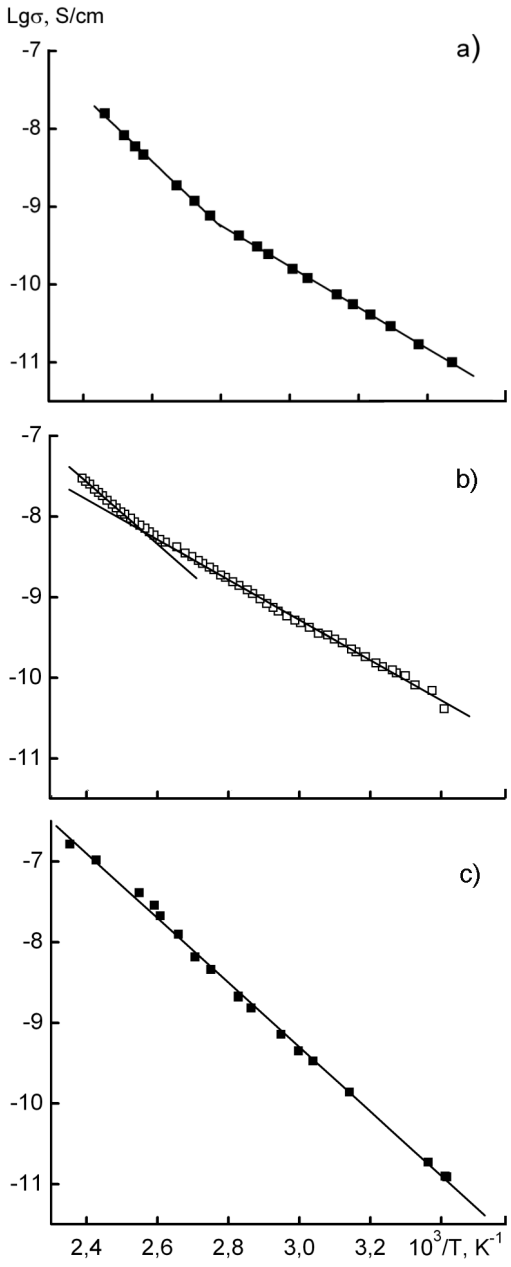

Fig. 1. Temperature dependences of conductance for KDP crystals ({101} growth sector) grown by recirculation (a, b) and temperature lowering (c) methods.

Table. Electric conductance parameters for pure and doped KDP crystals

Crystal	E_a (eV)	$\lg\sigma_0$ (S/cm)	σ_{RT} [c] (S/cm)	T (°C)	Notes	Ref.
KDP pure [a] (C1)	0.522±0.003	−1.87±0.06	$1.4\cdot10^{-11}$	<85	σ_{44} [f]	This work
KDP pure [b] (C1)	0.835±0.024	2.54±0.26	$1.5\cdot10^{-12}$	>85	σ_{44} [f]	This work
KDP pure [a] (C2)	0.520±0.005	−1.51±0.08	$3.6\cdot10^{-11}$	<130	$\sigma_{\|\|}$ [d]	This work
KDP pure [b] (C2)	0.796±0.009	2.1±0.1	$2.6\cdot10^{-12}$	130–145	$\sigma_{\|\|}$	This work
KDP pure [a,b] (C3A)	0.790±0.011	2.69±0.15	$1.3\cdot10^{-11}$	20–152	$\sigma_{\|\|}$	This work
KDP pure [a,b] (C3B)	0.710±0.022	1.10±0.33	$7.8\cdot10^{-12}$	20–100	$\sigma_{\|\|}$	This work
KDP pure [a]	0.54	−1.27	$2.8\cdot10^{-11}$	—	$\sigma_{\|\|}$	[22]
KDP pure [a]	0.49	−1.85	$5.3\cdot10^{-11}$	—	$\sigma_{\perp}$ [e]	—
KDP pure [a]	0.60	−0.59	$1.2\cdot10^{-11}$	50–100	$\sigma_{\|\|}$, ↑[g]	[4]
KDP pure [a]	0.61	−0.24	$1.9\cdot10^{-11}$	50–110	$\sigma_{\perp}$, ↑	—
KDP pure [a]	0.57	−0.6	$4.0\cdot10^{-11}$	50–110	$\sigma_{\perp}$, ↓[h]	—
KDP pure [b]	0.83	2.54	$1.9\cdot10^{-12}$	100–180	$\sigma_{\|\|}$, ↑	—
KDP pure [b]	0.85	2.9	$1.9\cdot10^{-12}$	110–180	$\sigma_{\perp}$, ↑	—
KDP pure [b]	0.67	1.0	$3.0\cdot10^{-11}$	50–180	$\sigma_{\perp}$, ↓	—
KDP pure [a]	0.55±0.01	−0.89±0.08	$4.5\cdot10^{-11}$	−40–180	$\sigma_{\|\|}$	[3]
KDP pure [b]	0.78±0.07	2.0±0.7	$3.9\cdot10^{-12}$	180–200	$\sigma_{\|\|}$	—
KDP pure [a]	0.540±0.004	−1.17±0.07	$3.5\cdot10^{-11}$	−40–180	$\sigma_{\perp}$	—
KDP pure [b]	0.78±0.07	2.0±0.9	$3.9\cdot10^{-12}$	180–200	$\sigma_{\perp}$	—
KDP:0.10 % SO_4 [a]	0.52±0.01	−0.3±0.3	$5.8\cdot10^{-10}$	20–100	$\sigma_{\perp}$	—
KDP:0.14 % SO_4 [a]	0.52±0.01	−0.2±0.2	$7.3\cdot10^{-10}$	20–110	$\sigma_{\perp}$	—
KDP:0.26 % SO_4 [a]	0.525±0.009	0.2±0.15	$1.5\cdot10^{-9}$	20–110	$\sigma_{\perp}$	—
KDP pure [a,i]	0.53±0.02	−1.73±0.04	$1.4\cdot10^{-11}$	20–100	$\sigma_{\|\|}$	[5]
KDP pure [b,i]	0.99±0.02	4.25±0.15	$1.7\cdot10^{-13}$	100–180	$\sigma_{\|\|}$	—
KDP pure [a]	0.55	−1	$3.5\cdot10^{-11}$	−40–180	—	[21]
KDP pure [b]	0.8	3.7	$8.8\cdot10^{-11}$	>180	—	—
KDP: CrO_4^{2-} [a]	0.54	3.2	$8.3\cdot10^{-7}$	−50–130	—	—
KDP: CrO_7^{2-} [a]	0.53	2.9	$6.1\cdot10^{-7}$	−50–130	—	—
KDP pure [a]	0.52	−2.16	$8.0\cdot10^{-12}$	30–120	$\sigma_{\|\|}$	[15]

[a,b] Low-temperature and high-temperature conductivity parameters, respectively. [c] The values of room temperature conductivity (σ_{RT}) were calculated using the parameters contained in the Table. [d,e,f] The values of conductivity in the parallel, perpendicular and at 44° directions relative to *c* crystal axis, respectively. [g,h] The temperature dependences were obtained at heating and at cooling of the crystal, respectively. [i] The conductivity was measured using the three-probe technique.

It follows from the temperature dependences of conduction using the Eq.(2) and data from Table that the conductivity of the crystals at T = 180°C is $(1.6–1.8)\cdot10^{-7}$ S/cm (C1, C2, C3B as well as the crystals used in [5]) or very close to those values $(2.0–2.8)\cdot10^{-7}$ S/cm (the crystals used in [3, 4]). This evidences that one and the same intrinsic conductance mechanism including the formation and migration processes of proton defects dominates in all the crystals under study in the high-temperature region [3-6].

As is seen in Fig. 1, the high-temperature conductivity of the C3A sample is higher than in other crystals. The sample mentioned has a rather high conductivity at room temperature, too, is spite of a high E_a value (Table). This fact indicates the presence of other conduction mechanisms in C3 with activation energy values within the $0.55<E_a<0.8$ eV range. Those mechanisms may be connected with the proton migration along interstices [6] at $E_a<0.8$ eV or with involvement of the proton defects associated with various crystal lattice imperfections in the conduction process. According to [6], the crystals with high E_a typical of intrinsic conduction mechanism are more perfect than those with low E_a typical of extrinsic conduction.

Among the crystals studied in this work, it is just C3 that has the highest activation energy and thus the most perfect. This is confirmed by the above chemical analysis data showing that the impurity content in C3 is lower than in C1 and C2. At the same time, the C1 and C2 crystal structures are more perfect than that of C3 in the crystal regions where there are no point defects responsible for the extrinsic conduction with E_a = 0.52 eV. This is confirmed by the fact that the conductivity of C1 and C2 crystals at room temperature ($1.5\cdot10^{-12}$ and $2.6\cdot10^{-12}$ S/cm, respectively), as determined from the high-temperature parameters E_a and $\lg\sigma_0$ using Eq.(2), is considerably lower than that of C3 at the same temperature (Table).

It follows from consideration of data from this work and other results that there is an interrelation between the electric conductance parameters. As is seen in Fig. 2 based on Table that there is a correlation between $\lg\sigma_0$ and E_a in the activation energy range 0.5–0.8 eV. The correlation coefficient K = 0.98. The low-temperature conduction parameters are interrelated as

$$lg\sigma_0 = k \cdot E_a + b, \qquad (3)$$

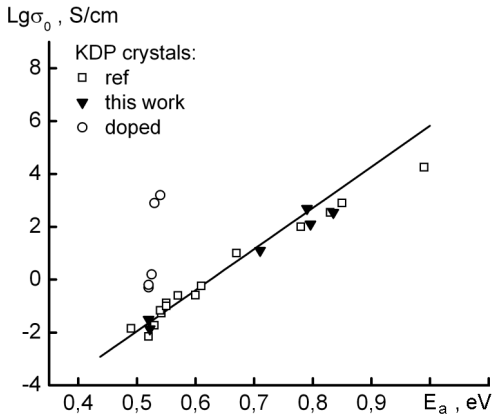

Fig. 2. Interrelation between the pre-exponential factor (σ_0) and conduction activation energy (E_a) in KDP crystals.

where k and b are constants. The values thereof calculated using least-squares method are k = 15.6±0.9 (S/eV·cm), b = –9.7±0.5 (S/cm).

The KDP electric conductance is almost isotropic [5], thus, the fact that the plot in Fig. 2 includes results obtained for different crystal directions is insignificant. The relationship (2) is found to be valid not only for KDP crystals studied in this work but also for those from other works [3–5, 15, 18, 21]. This testifies to the fact that all the crystals involve the same conduction mechanisms in spite of differences in the conduction parameters.

It is known [6] that the slope of regression line presenting the $\lg\sigma_0 = f(E_a)$ dependence in (E_a, $\lg\sigma_0$) coordinates depends on the disordering extent in the crystal. An increased curve slope corresponds to increased disordering at the formation of defects. This is connected with the fact that the quantity A in (1) is defined as $A = A_1\cdot\exp[\Delta S\cdot k]$, where ΔS is the entropy change; k, a constant. In our case, the experimental points (E_a, $\lg\sigma_0$) are almost in one and the same line in Fig. 2 representing the plot $\lg\sigma_0 = f(E_a)$. Thus, all the crystals characterized in Table have the same disordering extent at $T<100$°C.

In some instances, the relationship (3) is invalid. It is seen in Fig. 2 that the experimental points are deviated from the regression line at high activation energy values $E_a>0.8$ eV. This is connected with the fact that the intrinsic conduction mechanism (formation and migration of proton defects) dominates at those activation energy values. For the intrinsic mechanism (E_a ~ 0.8 eV),

the interrelation coefficients between σ_0 and E_a must have other numerical values than in E_a range 0.5–0.8 eV where both intrinsic and extrinsic conduction mechanisms play parts [6]. It is seen in Fig. 2 that the relationship (3) is not met for crystals with high concentrations of impurity ions SO_4 (above 0.1 %) [3], CrO_4^{2-} and CrO_7^{2-} [21]. This is due to the fact that incorporation of those ions causes an increased number of L-defects but does not result in any significant distortions of the crystal structure [3] and thus of the entropy, the increase of which causes an increased conduction activation energy E_a. At the same time, the increase of L-defect number in the crystals due to doping results in an increased electric conductance. This is reflected in a rise of the parameter σ_0 in Eq.(2) that depends not on the crystal disordering extent only but on the number of mobile defects affecting the conduction. That is the cause of the $\lg\sigma_0$ values deviation in heavily doped crystals from the regression line $\lg\sigma_0 = f(E_a)$ that occurs in this case mainly along the ordinate axis (Fig. 2).

The relationship (3) is not met for high-temperature conduction parameters [21] (Table) measured at T>180°C; perhaps that is connected with the crystal decomposition. It is known [21] that high temperatures affect heavily the physical properties of KDP crystals (due to transition into monoclinic phase) that become milky and opaque.

The deviations from the Eq.(3) may be due to macroscale defects, such as the structure distortions in some crystal areas (increased imperfection layers). Those are observable by the X-ray topography [6] in crystals grown from solutions having high pH values. It has been shown in the work mentioned that those defects cause a E_a reduction by 0.3 eV and room temperature conduction increase by several decimal orders.

It is seen from the above that the deviation of experimental points from the regression line (3) can be used as a criterion of the crystal quality.

To conclude, the temperature conductance dependences have been measured for KDP crystals (the {101} growth sectors) grown by recirculation and temperature lowering methods. The temperature dependences of conductance have been found to follow an exponential law of the Arrhenius type. The pre-exponential factor $\lg\sigma_0$, activation energy E_a and the conductivity value at room temperature have been determined. A correlation between the conduction parameters E_a and $\lg\sigma_0$ of undoped crystals exists within the activation energy range 0.49–0.79 eV that is observable in the 20–100°C temperature region.

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Особливості електропровідності монокристалів KDP

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В інтервалі температур 20–150°С досліджено електропровідність кристалів KDP, вирощених методом рециркуляції та методом зниження температури. Температурні залежності електропровідності підпорядковуються експоненційному закону. Визначено передекспоненційний множник та енергію активації електропровідності. Встановлено, що у недопованих кристалах у температурному інтервалі 20–100°С і діапазоні енергій активації 0.49–0,79 еВ існує кореляція між значенням логарифма передекспоненційного множника і енергією активації електропровідності. Коефіцієнт кореляції дорівнює 0.98. Це свідчить про те, що механізми електропровідності у кристалах з низькою концентрацією дефектів є аналогічними. Отримані результати обговорюються у рамках відомих моделей механізмів електропровідності в KDP, в основі яких є транспорт протона.