

Structural peculiarities and mechanical characteristics of KDP-family single crystals

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Investigated are mechanical characteristics of alkaline dihydrogen phosphate single crystals KH_2PO_4 and LiH_2PO_4 with different cation sizes. There are established those features of the internal structure that define the character of damage in the crystals under the mechanical stresses. It is shown that the mechanical strength of the studied crystals depends, first of all, on the number and direction of the hydrogen bonds in the crystal lattice. The longer hydrogen bonds ($\sim 2.684 \text{ \AA}$) in alkaline dihydrogen phosphate with a small four-coordinated cation $R_{\text{Li}^+} = 0.68 \text{ \AA}$ are weaker than the hydrogen bonds which belong to a strong type ($\sim 2.564 \text{ \AA}$) in alkaline dihydrogen phosphate with a large eight-coordinated cation $R_{\text{K}^+} = 1.33 \text{ \AA}$. The value of fracture toughness of LiH_2PO_4 single crystals is approximately 2-2.5 times lower than that of KH_2PO_4 single crystals. The plasticity of potassium dihydrophosphate is higher in comparison with the one of lithium dihydrophosphate. This is due to the fact that the contribution of the small Li^+ cation to the formation of the framework is lower than that of the large K^+ cation. The values of LiH_2PO_4 microhardness are 1.2-1.3 higher than the corresponding values of KH_2PO_4 .

Keywords: KDP- family, crystal structure, hydrogen bonds, hardness, fracture toughness.

Структурні особливості та механічні характеристики монокристалів групи KDP В.М. Баумер, О.Ф. Долженкова, І.М.Притула, А.М.Юрченко, О.І. Костенюкова

Вивчено механічні характеристики монокристалів лужних дигідрофосфатів з різним розміром катіонів KH_2PO_4 і LiH_2PO_4 . Встановлено, які особливості внутрішньої будови визначають характер руйнування під дією механічних напружень. Показано, що механічна міцність досліджуваних кристалів визначається насамперед кількістю та орієнтацією водневих зв'язків у ґратках. Більш довгі водневі зв'язки ($\sim 2.684 \text{ \AA}$) у лужному дигідрофосфаті з малим чотирикоординованим катіоном $R_{\text{Li}^+} = 0.68 \text{ \AA}$ більш слабкі, ніж водневі зв'язки, які відносяться до міцного типу ($\sim 2.564 \text{ \AA}$) у лужному дигідрофосфаті з великим восьмикоординованим катіоном $R_{\text{K}^+} = 1.33 \text{ \AA}$. Значення в'язкості руйнування монокристалів LiH_2PO_4 приблизно в 2-2.5 рази нижче, ніж значення в'язкості руйнування монокристалів KH_2PO_4 . Водночас пластичність дигідрофосфату калію вища, ніж дигідрофосфату літію, оскільки внесок малого катіона Li^+ до утворення каркасу є меншим, ніж у великого катіона K^+ . Значення мікротвердості LiH_2PO_4 в 1.2-1.3 рази перевищують відповідні значення мікротвердості KH_2PO_4 .

1. Introduction

The isoanionic crystals MH_2PO_4 ($M = \text{Li, Na, K, Cs}$) of alkaline dihydrogen orthophosphates have been investigated to a great extent. This family is best represented by KH_2PO_4 (KDP).

Potassium dihydrogen phosphate crystals are widely used in nonlinear optics, optoelectronics and laser technique due to their efficient quadric nonlinear optical (NLO) response, high resistance to laser-induced damage and the

possibility to grow large-size single crystals. At present KDP crystals are a unique material to be used for production of wide-aperture laser radiation frequency converters and Pockels cells for a new generation of ultra-power laser setups [1,2]. Lithium dihydrogen phosphate crystals LiH_2PO_4 (LDP) also belong to KDP-family, however, unlike KDP, lithium dihydrogen phosphate has no symmetry center, therefore these crystals are characterized by piezoelectric properties. LDP crystal lattice has a developed network of hydrogen bonds, thereby these crystals are proton conductors [3]. Lithium dihydrogen phosphate single crystals are characterized by an extremely high proton conductivity of $10^{-3} - 10^{-5} \Omega^{-1} \cdot \text{sm}^{-1}$, that makes them a promising material for electrochemical devices: efficient fuel cells, electrochromic display devices, proton batteries, solar energy storage and solid state dehumidifiers [4].

In [5] was studied the effect of cation size on the hydrogen bonding length and on the topology of coordination polyhedras of the series of anhydrous alkaline dihydrogen orthophosphates. The rise of cation size in the isoanionic series MH_2PO_4 ($M = \text{Li}, \text{Na}, \text{K}, \text{Cs}$) was shown to lead to increasing values of its coordination number, followed by “condensation” of cation polyhedral. An unambiguous decrease of hydrogen bonding length was also observed as the cation became larger.

Potassium dihydrogen phosphate single crystals KDP form a tetragonal system (space group $I 42 d$) at room temperature, with lattice parameters $a = b = 0.7452 \text{ nm}$, $c = 0.6972 \text{ nm}$, and $Z = 4$ [6].

Lithium dihydrogen phosphate single crystals LDP form an orthorhombic system of the space group $Pna2_1$ with $a = 0.6253 \text{ nm}$, $b = 0.7656 \text{ nm}$, $c = 0.6881 \text{ nm}$, and $Z = 4$ [7]. Hydrogen bonding shows quite similar topological features in the series of anhydrous alkaline dihydrogen orthophosphates. The PO_4 tetrahedra are linked by hydrogen bonds in all directions, so that three-dimensional frameworks are formed [5].

PO_4 tetrahedra in LDP are linked by two hydrogen bonds forming zigzag chains along $[100]$ and $[001]$. The size of lithium cations is $R_{\text{Li}^+} = 0.68 \text{ \AA}$, Li^+ ion shows the coordination number 4. Every lithium tetrahedron shares all its vertices with phosphorus tetrahedrons, so LiO_4 and PO_4 form isolated chains along the directions $[100]$. A three-dimensional network is formed by the chains of hydrogen bonds in the directions $[001]$ and $[100]$ [8] (Fig. 1).

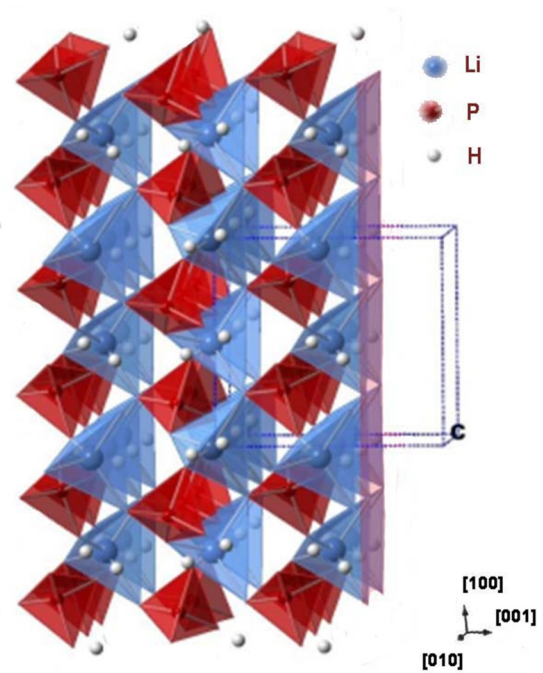


Fig. 1. Three-dimensional view of LDP crystal, structure, space group $Pna2_1$ [9].

The structure of KDP single crystals is a three-dimensional network of PO_4 tetrahedrons linked by the hydrogen bonds perpendicular to the direction $[0 0 1]$. Inside this framework there are located K^+ ions, with the size of potassium cations $R_{\text{K}^+} = 1.33 \text{ \AA}$. K^+ ion is characterized by the coordination number 8. Unlike LDP, in KDP crystals KO_8 polyhedrons and their neighbors have not only common vertices, but also common edges (Fig. 2). The framework of KDP is more complicated than that of LDP, the ionic bonds are involved in the structure formation to a greater extent than it takes place for LDP crystals [5,6].

The problems that arise during technical use of alkaline dihydrogen phosphate single crystals necessitate studying their mechanical characteristics. Several papers [10,11] have been devoted to the investigation of mechanical properties of KDP single crystals using indentation deformation. According to these studies, KDP crystals show indentation size effect in the range of loads between 0.24 and 1.96 N, and are characterized by a weak (12-20%) hardness anisotropy of the faces (001) and (100). LDP single crystals also possess reverse indentation size effect and minor anisotropy [12].

The method of indentation makes it possible to obtain the data not only on the micro-hardness of a material H that correlates with deformation parameters, but also the information

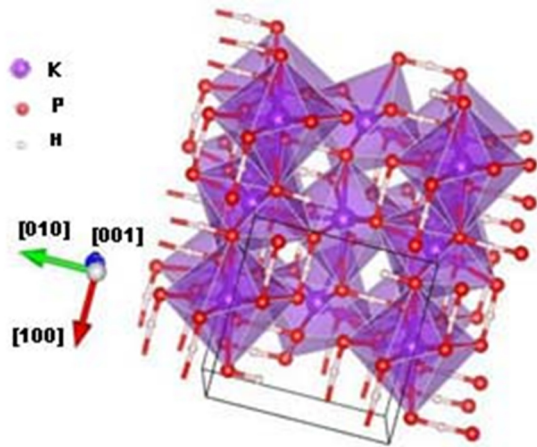


Fig. 2. Cell structure of KDP crystal, space group $I\bar{4}2d$.

concerning its fracture resistance. Namely, it allows to estimate the fracture toughness coefficient K_{1C} based on the length of radial cracks formed during indentation. There are known only single papers [12,13] devoted to the phenomenon of cracking in KDP and LDP crystals. These crystals which are soft and highly brittle materials have been shown to be characterized by strong anisotropy of properties. Therefore, KDP and LDP belong to gentle-brittle materials which are difficult to machine. The problems that arise during manufacture of elements from these single crystals necessitate further investigations of their mechanical characteristics. Moreover, at present there exist no works that elucidate the features of the internal structure of alkaline dihydrogen phosphate single crystals that define their breakdown mechanism under the influence of external factors.

The aim of the present work was to investigate the role of structure features in the formation of mechanical properties of the most representative alkaline dihydrogen phosphate crystals with different size of cation in KDP and LDP crystal structure.

2. Materials and methods

KDP crystals were grown from aqueous solution by the method of temperature reduction onto a point seed measuring $5 \times 5 \times 10 \text{ mm}^3$. The solutions were filtered and then overheated during 24 h at $T = 80 \text{ }^\circ\text{C}$. The relative solution supersaturation σ was $\sim 2\%$, the rate of temperature lowering being $0.3 \text{ }^\circ\text{C/day}$. To provide dynamical crystal growth conditions, the solution contained in the crystallizer was mixed at a rate of 70 rpm. The average crystal growth rates

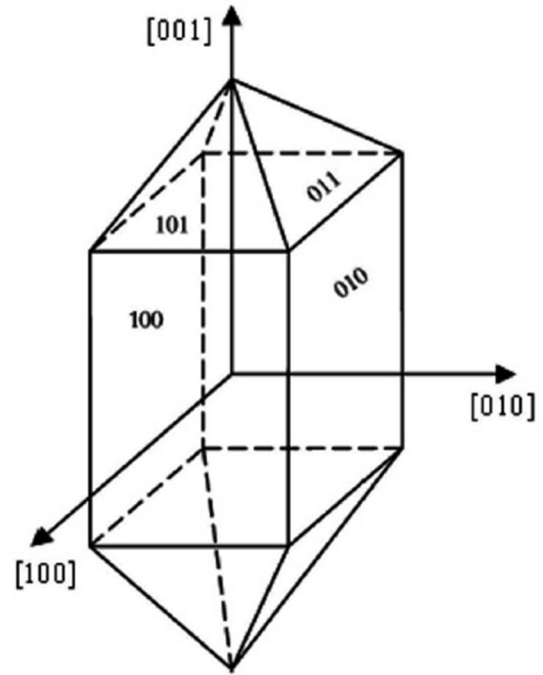


Fig. 3. Morphology of KDP crystal faces.

along the growth direction were $V_z = 2.0 \text{ mm/day}$ and $V_{x,y} = 1.3 \text{ mm/day}$. The dimensions of KDP crystal were $79 \times 65 \times 54 \text{ mm}^3$.

The morphology of KDP crystal is formed by tetragonal prism $\{100\}$ and tetragonal bipyramid $\{101\}$ faces. All the grown crystals had well-developed prismatic and pyramidal growth sectors (Fig. 3). The samples to be investigated were obtained from the pyramidal growth sector. The study was performed on the mechanically ground and polished faces (001) and (100) . Immediately before the experiments, the test surface was subjected to chemical polishing to remove the deformed layer formed during mechanical treatment of the samples.

LDP crystals were grown from aqueous solutions of orthophosphoric acid by the methods of solvent evaporation and temperature lowering [14,15]. LDP crystals with the dimensions $35 \times 27 \times 30 \text{ mm}^3$ were being grown over a period of 137 days from aqueous solutions containing 20% H_3PO_4 . The temperature of the acidic aqueous solution was lowered from 50 to $20 \text{ }^\circ\text{C}$. The crystal habit was defined by the pyramidal (111) and prismatic (110) faces. The tests were realized on the (110) and (111) as-grown faces of LDP (Fig. 4).

Mechanical characterization of the crystals was performed by means of Vickers microhardness tests. Indentation was realized using a PMT-3 device with the standard tetrahedral

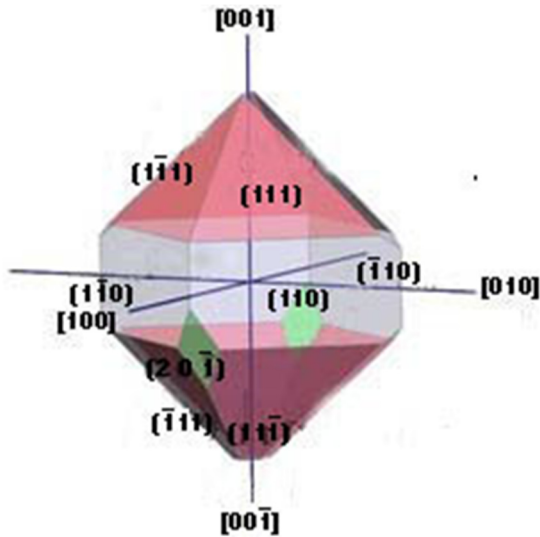


Fig.4. Morphology of LDP crystals grown from 20% H₃PO₄ solution [9].

indenter. The obtained indenter imprint and the radial cracks around it were measured by means of a computer-aided optical microscope Zeiss Axioskop 40A POL. The microhardness value was determined from the relation $H_V = 1854P_1/a^2$ (kgf/mm²), where P_1 is the indenter load (g), a , the imprint diagonal (μm). The crack resistance was evaluated by the residual stress intensity factor K_c according to the formula:

$$K_{1c} = 0.016 \cdot \left(\frac{E_1}{H_V} \right)^{1/2} \cdot \frac{P_1}{l^{3/2}} \quad (\text{MPa} \cdot \text{m}^{1/2}) \quad [16],$$

where l is the radial crack length from the indentation center to the crack tip, E_1 , the Young' modulus ($E_1 = 38.7$ GPa (KDP), $E_1 = 49.2$ GPa (LDP) [10,12]. The measurements were realized on 10 imprints at each indentation load applied. The standard deviation in the measured value of mean micro- hardness was about 2%, whereas this deviation in the average crack length was found to be up to 10%.

3. Results and discussion

The load-independent hardness ($P=0.75$ N) for the (001) face is somewhat higher than that for the (100) face - 1.95 GPa and 1.83 GPa, respectively. KDP single crystals are characterized by imperfect cleavage [17]. Radial cracks around the indenter imprint are observed at indenter loads starting from $P = 0.1$ N. Typical examples of the indentation imprints and cracks obtained on the planes (001) and (100) of

KDP at an applied load of 1 N are presented in Figs. 5 and 6. At the said load there is observed a developed system of radial cracks around the imprints. As the indenter creates a non-uniform stress field at indentation, the maximum cleavage stress develops at the imprint corners along the line that is a continuation of its diagonals. During indentation of the plane (001) (Fig. 5) the direction of the radial cracks coincides with that of the imprint diagonals when the latter are parallel to the directions [100] and [110]. As established while studying the brittle fracture zone on the face (001), the micro-cracks in the directions <100> approach the studied face at right angles. The micro-cracks in the directions <110> are the exits to the face (001) for the micro-cleavage planes located obliquely relative to the face under study. Besides the radial cracks, a developed system of lateral cracks parallel to the indented plane (001) is observed around the imprint.

Analysis of the cracking pattern obtained at applying load to the face (100) shows that the radial cracks from the imprint center are propagating in the directions [001] and [010], if the indenter diagonals are parallel to these directions (Fig. 6,a). At another indenter location (Fig. 6,b) the cracks are propagating along the direction [210]. The vertical crack along [001] and the horizontal crack along [010] approach the face (100) at right angle, whereas the crack along <210> approaches this face obliquely.

Joint consideration of the character of brittle fracture on the faces (001) and (100) caused by concentrated load and analysis of the crystallographic orientation of the cracks allows to conclude that micro-chipping in KDP crystals occurs parallel to the faces {221}, {001} and {001}. The cracks in the directions <110> on the face (001) and those in the directions <210> on the face (100) are the exits of the cleavage planes {221} on these faces. The crack on the face (100) in the direction [100] is identical to the side crack on the face (001). The crack along the direction [001] on the face (100) indicate the possibility of micro-cleavage along the planes {100}. The cracks along the directions <100> on the face (001) also testify to this fact. Most preferably the cracks are propagating parallel to the plane {221}, least preferred is (001).

The values of fracture toughness for the planes of easy crack propagation are are $K_c^{\{221\}} = 0.22 \text{ MPa} \cdot \text{m}^{1/2}$, $K_c^{\{100\}} = 0.33 \text{ MPa} \cdot \text{m}^{1/2}$, $K_c^{\{001\}} = 0.38 \text{ MPa} \cdot \text{m}^{1/2}$.

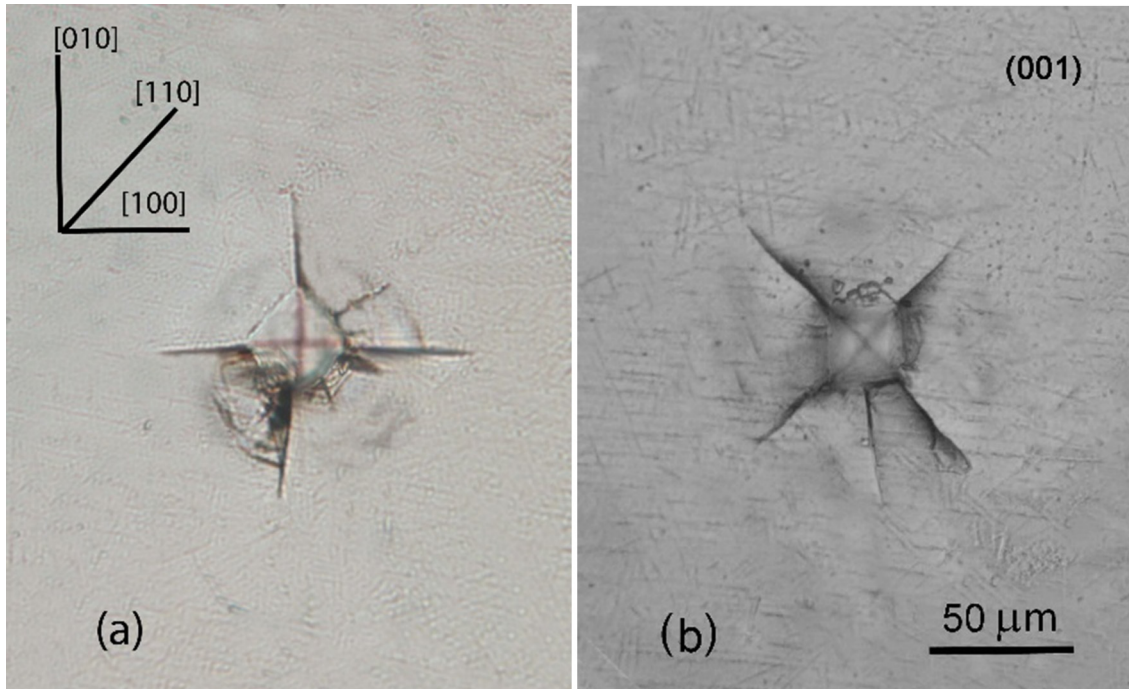


Fig. 5. Indentation imprints and cracks produced on (001) of KDP crystals at a load ($P = 1$ N). The indenter diagonals are parallel to the directions $[1\ 0\ 0]$ (a) and $[1\ 1\ 0]$ (b).

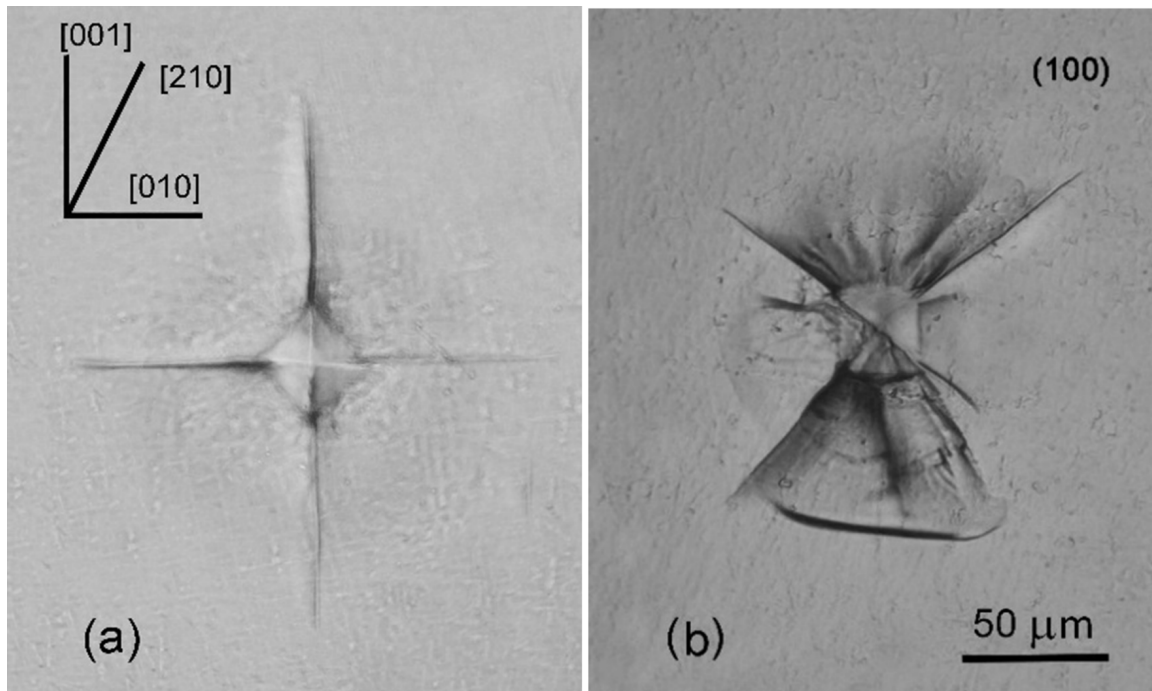


Fig. 6. Indentation imprints and cracks produced on (100) of KDP crystals at $P = 1$ N. The indenter diagonals are parallel to the directions $[01\ 0]$ (a) and $[01\ 1]$ (b).

Presented in Fig.7 are the projections of the structure of KDP single crystal on the planes (001), (100) and $\{221\}$.

These crystals are distinguished by the presence of different types of bonds between their atoms: covalent (internal bonds in PO_4 unit), hydrogen (O-H...O between adjacent

PO_4 units) and ionic (K-O) [6]. These bonds have different strength of interaction between the atoms. The strength of the chemical bond of P-O tetrahedron is 597 kJ/mol, the bond strength in K-O eight-vertex is about 239 kJ/mol. The hydrogen bonds are relatively weak, the strength of intermolecular hydrogen bonds is nearly 21 kJ/mol [10].

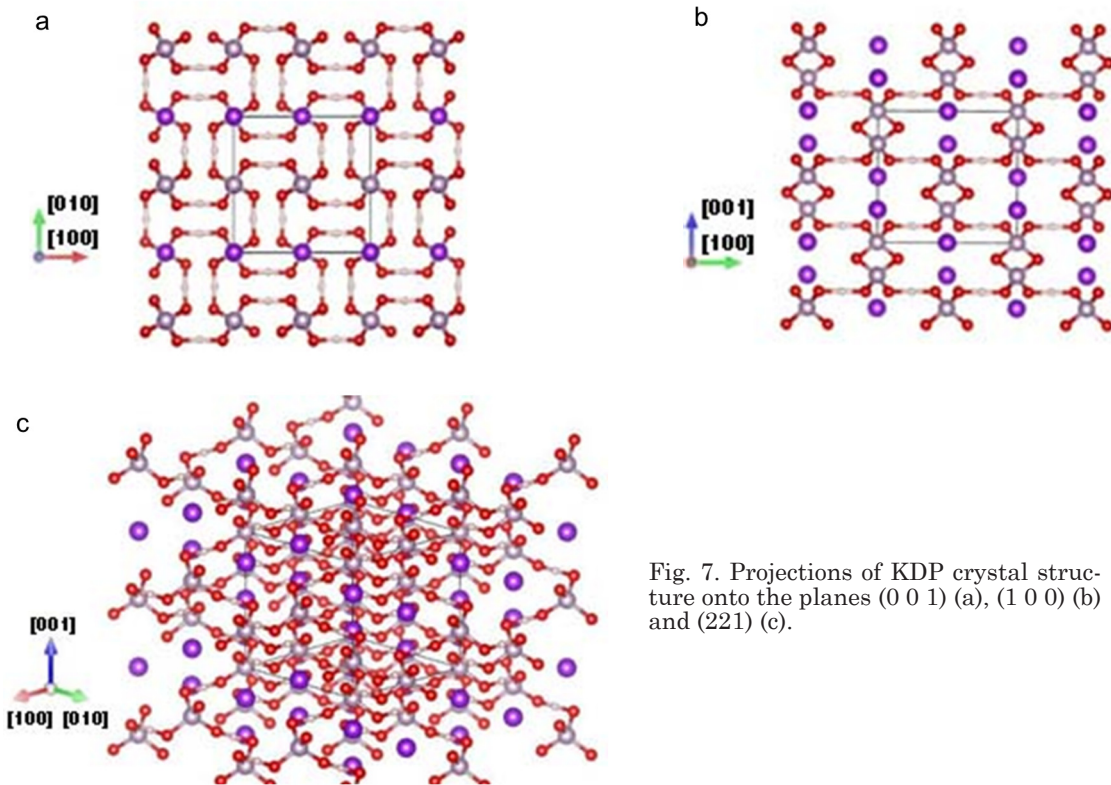


Fig. 7. Projections of KDP crystal structure onto the planes (0 0 1) (a), (1 0 0) (b) and (221) (c).

In KDP crystal structure the hydrogen bonds link PO_4 tetrahedrons into a three-dimensional framework. Each O ion from one PO_4 unit is linked with O ion from another PO_4 unit by hydrogen bond. The hydrogen bonds are parallel to the directions $[1\ 0\ 0]$ and $[0\ 1\ 0]$. In the gaps there are located K^+ ions, each of them is surrounded by eight O atoms belonging to PO_4 unit [6].

The character of destruction of the crystal under the action of a concentrated load depends on the type of crystal structure and the character of interatomic bonds. As is known, in the compounds with different types of bonds between the atoms, such as anhydrous alkaline dihydrogen orthophosphates, the strength is always defined by the weakest bonds [18]. Rupture of the layers of atoms parallel to the plane (001) is caused by breaking of the ionic bonds K-O that link these layers. Of the eight oxygen atoms that surround potassium ions, four are located closer to potassium ions than the rest. The ionic bonds K-O (with a length of 2.897 Å) are practically parallel to the axis z . The ionic bonds K-O (with a length of 2.824 Å) are practically perpendicular to the axis z . The shorter ionic bonds are located in the plane (001), the longer ones link the layers of atoms parallel

to the given plane. The crack along the plane (001) is propagating due to breaking of the longer K-O ionic bonds. In the given plane the value of crack resistance of the crystal reaches its maximum. Along the layers of atoms parallel to the plane (100) crack propagation is more preferred than that along the plane (001). In this case micro-cleavage is caused by breaking of weak hydrogen bonds between adjacent PO_4 units belonging to the lower and the upper layers. The maximum number of hydrogen bonds act between the planes $\{221\}$. In these planes crack propagation in KDP crystals is preferred.

As is known, the hydrogen bonds present in KDP single crystal play a very important role in NLO contributions to the total nonlinearity [19]. Therefore, the increase in the number of hydrogen bonds and optimization of their spatial arrangement in the crystal may be one of the methods for controlling its NLO characteristics. As established while studying the mechanical characteristics of KDP single crystal, its mechanical strength also depends, first of all, on the number and direction of weak hydrogen bonds in the crystal lattice.

The length of hydrogen bonds in the KDP family members is generally about 2.5 Å. In

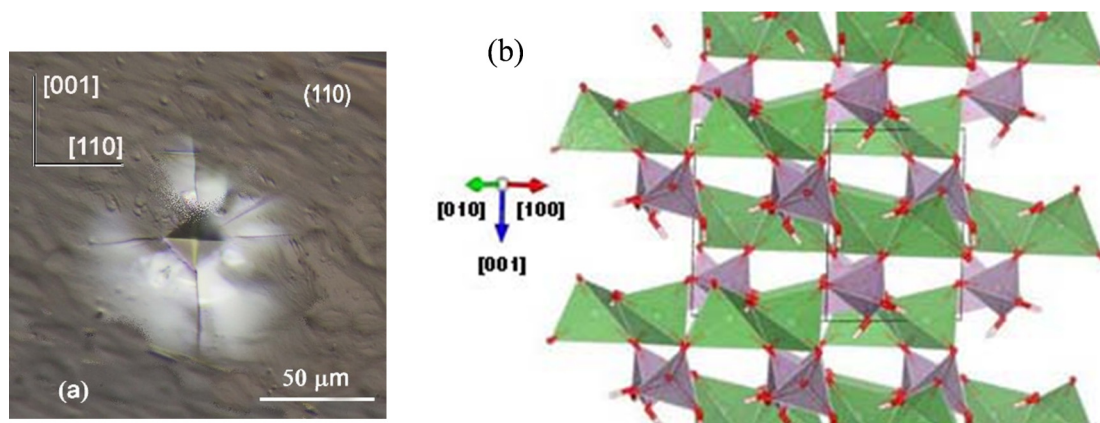


Fig. 8. Indentation imprint and cracks produced on (110) face of LDP crystal (a) and projection of the structure onto this plane (b).

the isoanionic series MH_2PO_4 ($M = Li, Na, K, Cs$) an unambiguous decrease was observed as the cation became larger. There were established the following lengths of the $O \cdots O$ hydrogen bridges in the structures: $NaH_2PO_4 - 2.500 \text{ \AA}$, $KH_2PO_4 - 2.494 \text{ \AA}$, $CsH_2PO_4 - 2.427 \text{ \AA}$ [5]. According to [20], $O-H \cdots O$ hydrogen bonding in solids is classified as strong, intermediate, or weak. There have been revealed two distinct types of hydrogen bonds in LDP. One of them, $O-H_1 \cdots O$, is the intermediate type ($\sim 2.684 \text{ \AA}$), in an asymmetric position along the [100]-axis. The other, $O-H_2 \cdots O$, belongs to the strong type ($\sim 2.564 \text{ \AA}$) in a general position forming an asymmetric bond along the [001]-axis [21]. A good proton conductor generally involves hydrogen bonds longer than 2.60 \AA as is the case for LDP, giving relatively weak hydrogen bond strength [22].

Analysis of the peculiarities of KDP and LDP crystal structures allows to assume that the strength and plastic characteristics of these crystals also will demonstrate both similarities and distinctions. Even if the crystal structures and symmetries of KDP and LDP are different, these compounds are mainly composed of M^+ cations ($M = K, Li$) and $H_2PO_4^-$ anions.

The load-independent hardness ($P=0.75 \text{ N}$) for the (110) and (111) faces is 2.16 GPa and 2.53 GPa , respectively. The value of microhardness obtained for LDP crystal approximately by ~ 1.2 - 1.3 times exceeds the corresponding values obtained for KDP crystal. The value of KDP plasticity exceeds that of LDP crystal. LiH_2PO_4 crystal contains isolated chains of Li^+ coordination tetrahedra linked by vertices. Since the same number of oxygen atoms must be accommodated by K^+ polyhedrons with a larger number of vertices, then condensation

of the polyhedr occurs by sharing vertices and edges. Thus, there arises a more complicated framework than the one in LDP [5]. The overall cationic contribution to the bond strength on the oxygen atoms may be significantly greater in KDP.

LDP crystals just like KDP are not characterized by cleavage. However, taking into account the character of bonds between the atoms in LDP and their direction, one should expect that this crystal will show micro-cleavage at applied local load. The planes (100) and (001) connected by hydrogen-bonded PO_4 groups are most weakly tied. Most likely, the cracks will be propagating along the given planes.

Presented in Figs. 8 and 9 are the indentation imprints and cracks obtained at an indenter load of 1 N on the planes (110) and (111). The figures also show projections of the crystal structure onto these planes. Care was taken to indent the two faces of crystal samples keeping the same indenter orientation on them. One of the indenter diagonals was oriented parallel to the projection of the direction [001] on the corresponding plane, the other was oriented along the direction [110] (Fig. 4).

During indentation of the plane (110) the direction of the cracks coincided with that of the imprint diagonals (Fig. 8,a). Some cracks originating from the opposite corners of the indentation imprint were not oriented strictly crystallographically and usually had different lengths. Around the imprint there appeared chipping, and along with the radial cracks, a developed system of lateral cracks parallel to the indented plane (110), was observed.

The indent pattern observed is defined by the character of bonding forces in LDP crystals on this plane (Fig. 8,b). The radial cracks

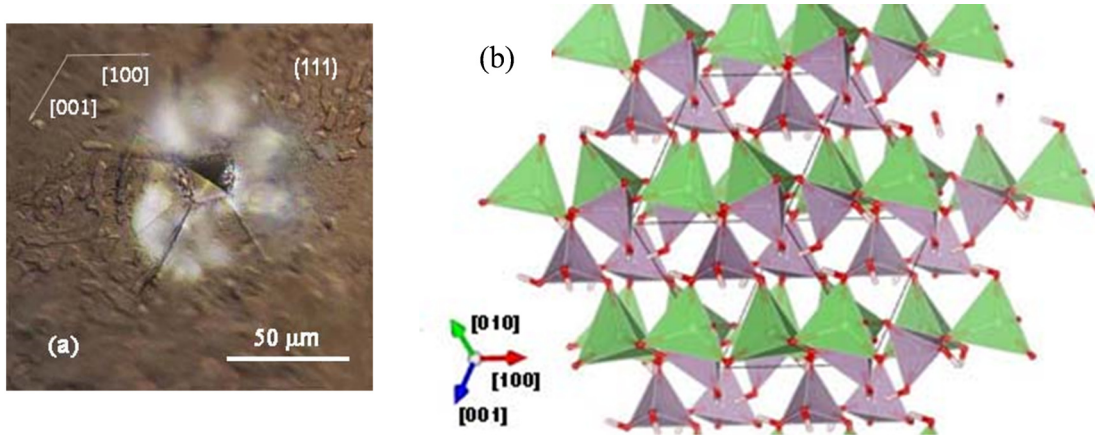


Fig. 9. Indentation imprint and cracks produced on (111) face of LDP crystal (a) and projection of the structure onto this plane (b).

parallel to the direction $[001]$ are propagating along the faces (100) inclined to the studied surface (110). The cracks parallel to $[110]$ formed during indentation are the exits of the micro-chipping planes $\{110\}$ to the studied face perpendicular to it. The presence of the side cracks parallel to the indented face further confirms that this plane is the plane of easy propagation of cracks. The hydrogen bonds O-H...O in the LDP structure are asymmetrical and form zigzag chains of the hydrogen-bonding PO_4 groups along the a- and c-axes. The hydrogen bonds are not strictly parallel to the $[100]$ and $[001]$ direction, therefore the cracks formed during indentation are propagating not only along the said directions, but also parallel to the direction $[110]$.

The cracks around the indenter imprints on the face (111) are propagating along the directions that correspond to the projections of the directions $[100]$ and $[001]$ on the studied plane (Fig.9,a,b). The said directions are the intersections of the planes (100) and (001) on the considered face. The indentation pattern shows that the most weakly linked planes - (100) and (001) – are micro-cleavage planes. Besides the radial cracks, a developed system of lateral cracks parallel to the indented plane (111) is observed around the imprint. Thus, the considered plane is also the micro-cleavage plane.

There are determined the values of fracture toughness for the micro-cleavage planes $K_c^{\{001\}} = 0.10 \text{ MPa}\cdot\text{m}^{1/2}$, $K_c^{\{100\}} = 0.12 \text{ MPa}\cdot\text{m}^{1/2}$, $K_c^{\{110\}} = 0.16 \text{ MPa}\cdot\text{m}^{1/2}$, $K_c^{\{111\}} = 0.18 \text{ MPa}\cdot\text{m}^{1/2}$.

The lowest value of fracture toughness is shown by the (001) plane. The layers of atoms parallel to the said plane are linked mainly by the strong hydrogen bonds connected to PO_4 groups. These layers demonstrate the least re-

sistance to breaking forces. The value of fracture toughness of the plane (100) is slightly higher than the one of the plane (001). Propagation of a crack along the plane (100) is due to rupture of weak intermediate hydrogen bonds. However, in this case the ionic bonds in lithium tetrahedrons forming $[100]$ isolated chains, which are much stronger than the hydrogen ones, are also broken. The values of fracture toughness for the (110) and (111) planes exceed similar values for the (100) and (001) planes. Between the layers of atoms parallel to the faces (110) and (111) there exist predominantly the Li-O ionic bonds, their quantity exceeds that of weak hydrogen ones. In this case the breaking resistance is maximum.

The value of fracture toughness of LDP single crystals is approximately 2-2.5 lower than the corresponding value for KDP single crystals. A lower crack resistance of LDP is bound up with the differences in the structure of these crystals considered above. A three-dimensional network of LDP is formed by the chains of relatively weak hydrogen bonds in the $[001]$ and $[100]$ directions. The contribution of the small Li^+ cation to the formation of the framework is smaller than that of the large K^+ cation.

4. Conclusions

KDP crystals were obtained by means of the method of temperature reduction onto a point seed, LDP crystals were grown from aqueous solutions by the method of solution evaporation. The mechanical properties of the crystals were investigated by micro-indentation hardness testing using a Vickers indenter tip. Indentations were made on the (001) and (100) faces of KDP crystals and on the (110) and (111) faces of LDP crystals. The value of micro-hard-

ness of KDP ($H^{(001)} = 1.95$ GPa и $H^{(100)} = 1.83$ GPa) is lower than the corresponding values of LDP crystals ($H^{(110)} = 2.16$ GPa and $H^{(111)} = 2.53$ GPa). The value of crack resistance of KDP crystals exceeds that of LDP crystals. The obtained values are the following: $K_c^{\{221\}} = 0.22$ MPa·m^{1/2}, $K_c^{\{100\}} = 0.33$ MPa·m^{1/2}, $K_c^{\{001\}} = 0.38$ MPa·m^{1/2} (KDP) и $K_c^{\{001\}} = 0.10$ MPa·m^{1/2}, $K_c^{\{100\}} = 0.12$ MPa·m^{1/2}, $K_c^{\{110\}} = 0.16$ MPa·m^{1/2}, $K_c^{\{111\}} = 0.18$ MPa·m^{1/2} (LDP). It is shown that the differences in the mechanical characteristics of the investigated crystals are bound up with the peculiarities of their internal structure. The three-dimensional frameworks are formed by PO₄ tetrahedrons connected by hydrogen bonds in all directions. Alkaline dihydrogen phosphate with small four-coordinated cation $R_{Li}^+ = 0.68\text{\AA}$ involves the hydrogen bonds longer than 2.60\AA giving relatively weak bond strength. The compounds with a large cation are characterized by the strong shortest hydrogen bonds. In alkaline dihydrogen phosphate with large eight-coordinated cation $R_K^+ = 1.33\text{\AA}$ the ionic bonds are to a greater extent involved in the formation of the structure than in the case of LDP crystals. KDP single crystals are characterized by a higher plasticity, the values of micro-hardness of the given single crystals are slightly lower than those of LDP. Crack propagation in alkaline dihydrogen phosphate crystals occurs, first of all, due to breaking of directional hydrogen bonds as well as of ionic bonds. The values of fracture toughness of LDP single crystals are essentially lower than those of KDP single crystals.

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