Effect of thallium impurity on the growth kinetics and perfection of KDP crystals

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The influence of Tl^+ ion isovalent impurity on growth kinetics of prism {100} and pyramid {101} sides of ADP ($NH_4H_2PO_4$) crystals is investigated as well as the influence of growth conditions on formation of the macrosteps on growing faces and structural perfection of crystals. The presence of thallium impurity in the solution results in the "dead zone" enlarged towards the area of increased overcooling (supersaturation). The values of face growth rates both for the prism and the pyramid do not change essentially. Using three-crystal X-ray diffractometry, diffraction reflection curves (DRC) from the {100} and {101} growth planes have been obtained. The DRC fragmentation is revealed caused by formation of growth macrosteps during blocking of elementary step progression by the impurity occurrence. The growth on the {100} plane is realized by formation of larger growth macrosteps than on the {101} one. The normal growth rate of the {100} plane exceeds almost twice that for {101} one. The Tl^+ impurity is mainly adsorbed at the {100} crystal face. The distribution coefficient of Tl^+ impurity for {100} and {101} planes is shown to differ twice being 1.0 and 0.5, respectively. Thallium impurity within the concentration range $C_{Tl} \leq 1$ wt. % does not affect essentially the structural perfection of doped ADP crystals.

Исследовано влияние изовалентной примеси ионов Tl+ на кинетику роста граней призмы (100) и пирамиды (101) кристаллов ADP ($NH_4H_2PO_4$), и влияние условий выращивания на формирование макроступеней роста и структурное совершенство кристаллов. Наличие примеси таллия в растворе приводит к увеличению "мертвой зоны". При этом не меняются существенно сами величины скоростей роста граней призмы и пирамиды по сравнению с чистым кристаллом. Нормальная скорость роста плоскости (100) почти в два раза больше, чем для плоскости (101). Методом трехкристальной рентгеновской дифрактометрии исследовано структурное совершенство легированных кристаллов, получены кривые дифракционного отражения (КДО) от плоскостей роста (100) и (101). Обнаружено дробление КДО, обусловленное образованием макроступеней роста при блокировании продвижения элементарных ступеней вхождением легирующей примеси. Рост на плоскости (100) осуществляется образованием более крупных макроступеней роста, чем на плоскости (101). Примесь Tl^+ преимущественно адсорбируется на грани (100) кристалла. Показано,что коэффициент распределения примеси Tl^+ для плоскостей (100) и (101) отличается в два раза: 1.0 и 0.5, соответственно. Примесь таллия в пределах концентраций ($C_{Tl} \leq 1$ мас.%) не оказывает существенного влияния на структурное совершенство легированных кристаллов ADP.
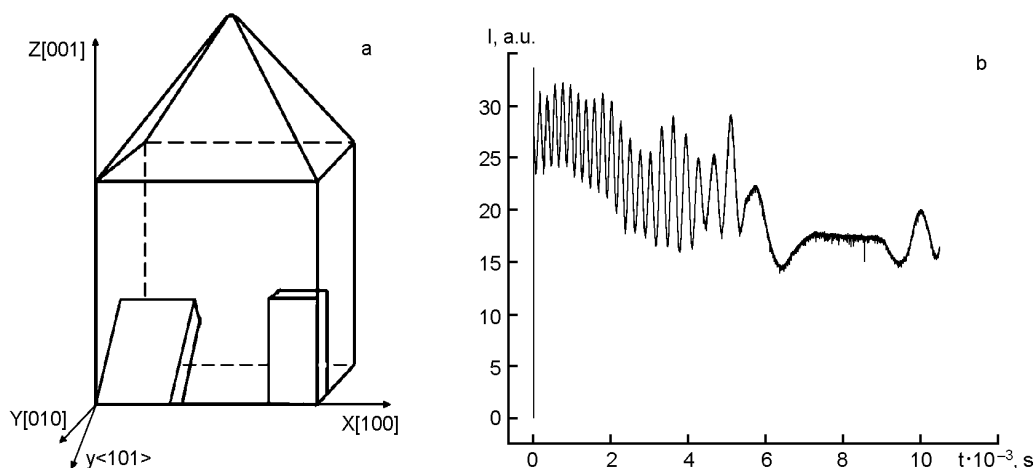
Fig. 1.Scheme of the seed preparation (a). Variation of the passed beam intensity with the crystal thickness (b).

1. Introduction

The growth and properties of water-soluble KDP and ADP crystals (potassium and ammonium dihydrophosphates) alloyed with various inorganic and organic impurities [1-5] are under active investigation during last few years. So, for example, nonlinear-optical ADP crystals alloyed with l-arginine hydrochloride and l-alanine improve the crystal perfection [1]; potassium chloride and oxalic acid enhance the 2nd harmonics generation [2]; cobalt and DL-malic acid improve the crystal dielectric propereties (the d_{33} value is twice higher for cobalt-doped crystals and four times higher for the acid-doped ones that for pure crystals [3]); the co-doping with nikcel and magnesium ions increases the transmission coefficient in visible spectral area [4, 5]; nonlinear-optical ADP crystals alloyed with thallium ions get luminescent and scintillation properties [6].

Numerous researches of an impurity influence on KDP and ADP crystals growth are known. It has been found that the growth of prism (100) faces and pyramid (101) ones differs essentially [7]. "The dead zone" area (the solution oversaturation range where the growth is absent) is revealed for the prism (100) sides at low solution supersaturation. The higher is the impurity concentration, the larger is the "dead zone" [8, 9]. During increase of supersaturation and the beginning of growth, a trend to formation of macrosteps [10, 11] and capture of inclusions from the solution [12] is shown. In KDP, the heterovalent metal impurities (Fe^{3+}, Cr^{3+}, Al^{3+}) are captured actively at the prism face, the distribution factors reaching values of the order of 10

[13]. The influence of impurities on growth of pyramid faces {101} is much weaker, and the distribution factors amount about 0.1 [14]. In ADP, the segregation of chromium impurity between the prismatic and pyramidal growth segments is observed, the distribution coefficients reach a value close to inuty [15]. In [16], the growth kinetics violation due to the dislocation source activity was studied. In this case, strong variations in different types of the growth rate dependence on oversaturation was observed. The effect of chromium impurity on the source activity is ascribed to the free energy change of the step butt.

Thus, there is some information on influence of heterovalent impurities on growth of the prism and pyramid faces of ADP crystals. However, that information is insufficient. In this work, presented are the study results of the growth kinetics and structure perfection of ADP crystals doped with isovalent Tl^{+} impurity.

2. Experimental methods

The kinetics of an ADP crystal growth was investigated using an interference-polarization setup [17] on from aqueous solutions under stirring. The normal growth speed of a seed shaped as a plate $x \times y \times z = 5 \times 1 \times 10$ mm^3 size was calculated proceeding from the time- dependent grown layer thickness measured *in situ*. The preparation scheme for the (100) and (101) oriented seeds is shown in Fig. 1. The seed was placed in a temperature-controlled optical cell. The solution in the cell was stirred by a magnetic mixer. The solution temperature was changed at a rate 0.01°C/min and meas-
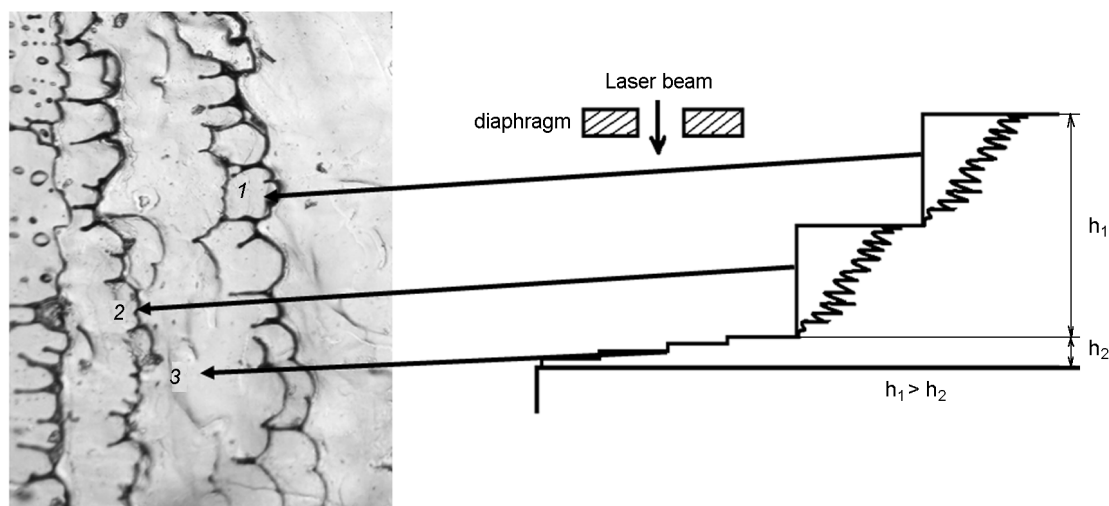
Fig. 2. Model of the macrostep motion at the crystal increase: *1, 2*, the macrostep end faces; *3*, terrace between the macrosteps moving sequentially.

ured with a DS18B20 digital thermometer. A beam of a semiconductor laser with $\lambda = 0.65\mu$m was passed through the growing crystal perpendicularly to the crystal optical axis. Polarization of the laser light made an angle of $45°$ with the crystal optical axis. The passed laser beam intensity varying due to interference of the ordinary and unusual beams according to a sine law is connected with known ratio with thickness of the crystal [18]. A typical time dependence of the transmitted beam intensity I is shown in Fig. 1. The linear section on the sinusoid corresponds to time during which no growth or dissolution of a crystal is fixed, the solution temperature being changing. The values of intensity I and temperature were recorded every second. Taking into account that the crystal dissolution speed exceeds by 5-6 times the growth rate [19], the temperature of solution saturation will correspond to temperature distant 1-2 min from the termination or the onset of change in the passed beam intensity from the side of the sinusoid section showing the crystal dissolution.

The normal growth speed for one half-cycle of intensity change is expressed as:

$$R = \frac{\Delta d}{2\Delta t} = \frac{\lambda}{4\Delta n} \cdot \frac{1}{\Delta t}\left[\frac{\mu m}{min}\right] \qquad (1)$$

where Δd — is the crystal thickness change (increase); $\Delta n = n_o - n_e = 0.044472$ for $\lambda = 0.65$ μm, n_0, n_e being the basic refractive indices of ADP crystal [20]; Δt, the sinusoid change time intensity for one half-cycle (halved, since two planes of the growing

seed are transmitted by the laser). The values of growth rate R calculated according to (1) for each half-cycle of experimental dependence of the passed laser beam intensity change, Fig. 3, and synchronized with change of the solution temperatures made it possible to construct the dependences of growth rate of prism (100) and pyramid (101) faces on the solution overcooling $\Delta T = T_{sat} - T_{sol}$ for nominally pure ADP crystals and for those alloyed with thallium. The impurity was introduced into the solution as $TINO_3$ salt at the rate of 1 wt. % of Tl^+ ions. The crystals were grown both at decrease in temperature from the solution saturation point and at the solution heating from overcooled state up to the saturation point. The structural perfection of samples was studied using the three-crystal X-ray diffractometry (TXD) [21]. The crystal surface *ex situ* was observed using an "Axioskop 40" microscope (Zeiss).

3. Discussion of results

The obtained values of $R(\Delta T)$ form curves where sections are possible to select with monotonous $R(\Delta T)$ dependence and sharp spasmodic change of growth rates when passing from one section to another. It is possible to explain such spasmodic changes of growth rate assuming the formation of growth macrosteps at the growing surface [22]. Really, if to examine *ex situ* the crystal surface morphology, the distribution of macrosteps from a dislocation source or an edge between the prism and the
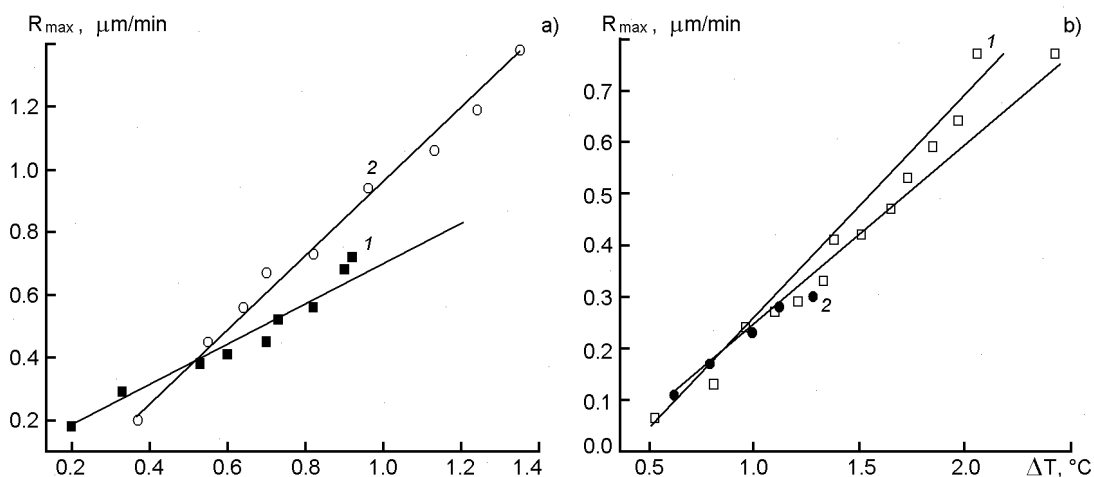
Fig. 3. Averaged dependences of the growth rate R_{max} on the solution overcooling ΔT for "pure"(*1*) and Tl doped (*2*) ADP crystals: (a) for prism faces, (b) for pyramid faces.

pyramid faces is seen even at small magnification in an optical microscope. The probable model of observable growth rate spasmodic changes is shown in Fig. 2: the laser beam passing through the growing crystal is limited to the diaphragm with an aperture of 1 mm in diameter, therefore, the extending macrosteps cross the exposed area already having a certain thickness that we observe as a jump of growth rate.

Then the crystal thickness on the plateau between consequently moving macrosteps increases monotonously, obviously due to movements of elementary growth steps or smaller macrosteps unresolvable in our method of measurement of the crystal thickness (≤ 0.2 mm). These growth rate values are seen as the monotonous $R(\Delta T)$ dependence inside the section. These dependences show the form $R \sim \beta(\Delta T)$, that is, the growth rate depends linearly on the solution overcooling The slope of $R(\Delta T)$ in each section increases with increasing overcooling, i.e. with the increase of ΔT the kinetic factor of macrosteps and the growth rate R increase from one section to another.

From the plots of $R(\Delta T)$ dependences similar to those shown in Fig. 2, averaged dependences $R_{max}(\Delta T)$ are constructed, where R_{max} is the maximum growth rate in each section corresponding to the moment of crossing of the laser beam with an end face of the macrostep (the moment of crystal thickness jump). The dependences of maximum growth rates R_{max} on the solution overcooling for faces of the prism and pyramid for ADP crystals, both pure and alloyed with thallium are presented in Fig. 3.
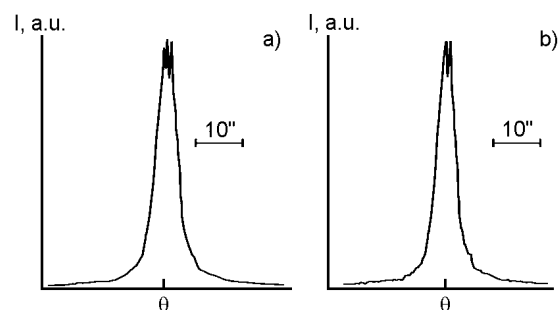

Fig. 4. Diffraction reflection curves obtained using TXD in $CuK_{\alpha 1}$ emission: (a) (101) face, reflection (404); (b) (100) face, reflection (800).

These values are seen to be on a straight line beginning immediately from the "dead zone", thus pointing to the displacement of macrosteps [9]. The thallium impurity presence in the solution displaces "dead zone" to the area of increasing overcooling. For the (100) face, "the dead zone" is displaced in interval $\Delta T_M = (0.2 \rightarrow 0.35)°C$, and for (101) one, the displacement $\Delta T_M = (0.5 \rightarrow 0.6)$ °C. That is, the prism face is more sensitive to presence of thallium impurity in the solution than that of the pyramid, thus, a higher overcooling is required for the prism face growth.

Comparison of growth rates of the prism and pyramid faces has shown that the (100) face grows approximately twice so fast than the (101) one, the supersaturation being the same. At the same time, thallium impurity does not change essentially the growth rate values as such (the difference does not exceed 15 or 20% within the studied concentration limits, $C_{Tl} \leq 1$ wt. %), i.e. growth rate of the prism and the pyramid faces
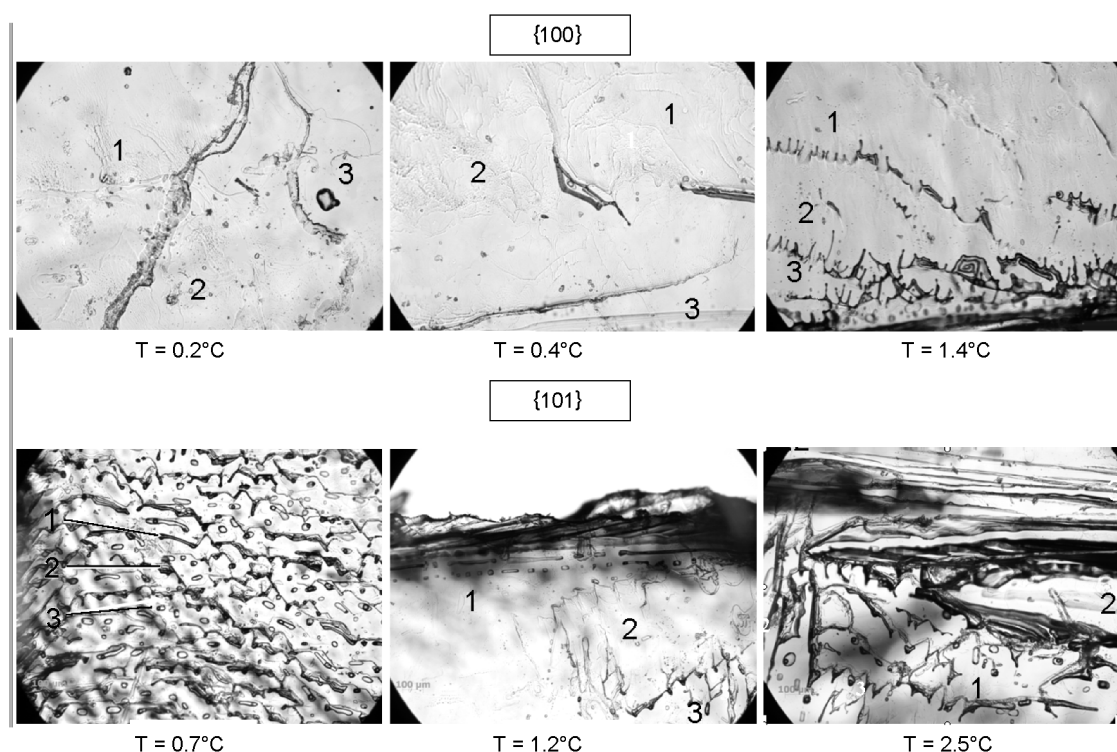
Fig. 5. *Ex situ* image of the growth macrosteps arrangement on (101) and (100) faces of Tl doped ADP crystals depending on the solution overcooling: *1*, *2*, *3*, designation of macrosteps moving sequentially from the dislocation source.

does not depend on the presence of thallium impurity in the solution. Such feature can be explained by a sharp change in the dislocation source activity at the (100) face due to formation of macrosteps. Since the step density and thus the growth rate on the dislocation hikkock is in proportion to the total Burgers vector, the increasing activity of the dislocation source should be accompanied by the appearance of fast-growing growth hillocks [16].

During the crystal growth, formation and movement of macrosteps is reflected in distribution of impurities and internal pressures in the crystal [23]. The influence of thallium impurity on structural perfection of ADP crystals was estimated using a three-crystal X-ray diffractometer using the diffraction reflection curves (DRC). The DRC from growth planes (100) and (101) for pure and alloyed ADP crystals were obtained. The diffraction reflection curves in Cu $K_{\alpha 1}$ radiation are presented in Fig .4: a) face (101), reflex (404), b) face (100), reflex (800). The curves show fragmentation of diffraction peak, larger number of peaks is observed for (100) faces. The reason for DRC fragmentation are small-angle rotations of vicinal reflection planes caused by

formation of growth macrosteps (packages of growth layers) at blocking promotion of elementary steps by the impurity introduction. In microphotos *ex situ*, Fig. 5, distinction in arrangement of (100) and (101) growth steps at identical growth conditions are seen. At the (100) face, the trend to grouping and formation of macrosteps is observed, where the height increases and interstep distance decreases with increasing overcooling. As to the (101) face, homogenization of steps is observed to a greater extent, the macrosteps appear only at overcooling exceeding 2.5°C. Thus, planes (100) tend to form larger growth macrosteps than (101) ones. As to thickness of a growing plate, the growth macrosteps have regular distribution at single-sector growing with plane (101). The average size of growth layer packages (macrosteps) makes 10 to 15 µm. The *ex situ* microphotos of (100) and (101) growth surfaces of thallium-alloyed ADP crystals are presented in Fig. 5.

According to [24], the impurity adsorption on the (101) pyramid face is hindered by the charge state of the growth surface. The prism plane (100) during the growth is formed by phosphate-ammotium packages

and has no electric charge while NH_4^+ ions form the (101) plane that is charged positively. The neutral (100) plane is always open to thew interaction with cationic impurity; in contrast, the positive charge of the (101) one hinder the adsorption and introduction of positive ions. It is found that Tl^+impurity is adsorbed on the (100) crystal face to a greater extent, that is confirmed by higher distribution factor of Tl^+impurity for planes (100) as compared to thev (101) one (1.0 and 0.5, respectively) as well as by more essential change of the crystal lattice parameters. Tl^+ions are isovalent to ammonium NH_4^+ ones and their ionic radii are close together ($r_{Tl^+} = 1.45$ Å; $r_{NH_4^+} = 1.48$ Å [25]), the ionic radius mismatch is less than 2%, so thallium substitutes easily the ammonium group. The difference in thallium introduction factors into the prism and pyramid growth segments is explained by the charge state of the growth surface. The high-precision measurements of the crystal lattice parameters a and c in crystals with thallium concentration of 1 wt % show that the parameter a is increased by $\Delta a = 9 \cdot 10^{-4}$ Å while c is decreased by $\Delta c = 11.2 \cdot 10^{-4}$ Å. The structure perfection of alloyed ADP crystals was estimated basing on the rocking curve half-width β. The β values are within 7-10 arcsec range for all investigated values of thallium concentration, thus evidencing a high structure perfection of the crystals. No essential changes of integrated X-ray reflection capacity, I_{cap}^R, was found, that first of all show a low density of bidimensional defects of crystal lattice. Scanning of a sample with X-ray beam has shown uniformity of structure perfection over the section of the grown crystals.

4. Conclusions

The presence of isovalent Tl^+ impurity in the solution ($C_{Tl} \leq 1$ wt. %) enlarges the "dead zone". At the same time, thallium impurity does not change essentially (to within 15-20%) the growth rates as such of the alloyed crystals as compared to the "pure" ones. In the presence of thallium, the growth gate change is more appreciable for the (100) plane as compared to the (101) one that can be explained by a sharp change of the diclocation source activity at the (100) plane due to macrostep formation. The presence of macrosteps is confirmed both by three-crystal X-ray diffractometry and by direct observation of the surface morphology in optical microscope. In the diffraction reflection curves, the diffraction peak fragmentation is revealed due to formation of the growth macrosteps (the growth layer packages) under blocking the elementary steps due to the impurity entering. During the crystal growth, larger growth macrosteps are formed at the (100) plane than at the (101) one. Tl^+ impurity is adsorbed on the face {100} to a greater extent, thallium substitutes ammonium group under account for the charge state of the growth planes. This results in a difference in the thallium entering coefficient in the prism and pyramid growth segments (1.0 and 0.5, respectively). Within the limits of the studied concentration, no essential influence of thallium impurity on structural perfection of alloyed ADP crystals is determined.

References

1. P.V.Dhanaraj, G.Bhagavannarayana, N.P.Rajesh, *Mater. Chem. and Phys.*, **112**, 490 (2008).
2. G.Bhagavannarayana, S.Parthiban, S.Meenak-shisundaram, *Cryst. Growth & Design*, **8**, 446 (2008).
3. P.Rajesh, P.Ramasamy, B.Kumar, G.Bhagavan-narayana, *Physica B*, **405**, 2401 (2010)
4. A.Claude, V.Vaithianathan, R.Bairava Ganesh et al., *J.Appl.Sci.*, **6**, 85 (2006).
5. P.Rajesh, P.Ramasamy, C.K.Mahadevan, *Mater. Lett.*, **64**, 1140 (2010).
6. A.P.Voronov, V.I.Salo, V.M.Puzikov, *Kristal-lografia*, **51**, 742 (2006).
7. L.N.Rashkovich, KDP Family Single Crystals, Adam-Hilger, New York, (1991).
8. A.T.Amandosov, S.S.Parshina, L.N.Rashk-ovich, *Kristallografia*, **10**, 469 (1983).
9. A.A.Chernov, L.N.Rashkovich, A.A.Mkrtchan, *Kristallografia*, **32**, 737 (1987).
10. A.A.Chernov, Yu.G.Kuznetsov, I.L.Smolsky, V.N.Rozhansky, *Kristallografia*, **31**, 1193 (1986).
11. J.Foncuberta, R.Rodrigues, J.Tejada, *J. Cryst. Growth*, **44**, 593 (1978).
12. N.Zaitseva, L.Carman, *Prog. Cryst. Growth and Charact. Mat.*, **43**, 1 (2001).
13. N.Zaitseva, I.Smolsky, L.Carman, *J. Cryst. Growth*, **222**, 249 (2001).
14. I.Smolsky, J.J.De Yoreo, N.Zaitseva et al., *J. Cryst. Growth*, **169**, 741 (1996).
15. S.Gits, M.C.Robert, F.Lefaucheux, *J. Cryst. Growth*, **71**, 203 (1985).
16. P.G.Vekilov, Yu.G.Kuznetsov, *J. Cryst. Growth*, **119**, 248 (1992).
17. L.N.Rashkovich, V.G.Leschenko, N.M.Sadykov, *Kristallografia*, **27**, 966 (1982).
18. G.S.Lansberg, Optics, Nauka, Moscow (1964) [in Russian].
19. I.L.Smolsky, A.P.Malkin, *Kristallografia*, **31**, 769 (1986).

20. Acoustic Crystals, ed. by M.P.Shaskolskaya, Nauka, Moscow (1982) [in Russian].
21. V.M.Puzikov, V.I.Salo, M.I.Kolybaeva et al., KDP/DKDP Single Crystals for High-Power Lasers: Growing, Properties, Appications, Inst. for Single Crystals Publ., Kharkiv (2004) [in Russian];
22. T.A. Land, J.J. De Yoreo, T.L. Martiu, *Crystallography Reports*, **44**, 655 (1999)
23. V.M.Puzikov, V.F.Tkachenko, V.A.Tsurikov, *Functional Materials*, **15**, 556 (2008).
24. S.A.De Vries, P.Goedtkindt, S.L.Bennet et al., *Phys. Rev. Let.*, **80**, 2229 (1998).
25. G.B.Bokiy, Crystal Chemistry, 3rd ed., Nauka, Moscow (1971) [in Russian].

Вплив домішки талію на кінетику росту та досконалість структури кристалів ADP

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Досліджено вплив ізовалентної домішки іонів Tl^+ на кінетику росту граней призми (100) та піраміди (101) кристалів ADP ($NH_4H_2PO_4$), та вплив умов вирощування на формування макроступенів росту та структурну досконалість кристалів. Наявність домішки талію у розчині спричиняє збільшення "мертвої зони". При цьому істотно не змінюються самі значення швидкостей росту граней призми та піраміди у порівнянні з чистим кристалом. Нормальна швидкість росту площини (100) майже вдвічі більше, ніж для площини (101). Методом трикристальної рентгенівської дифрактометрії досліджено структурну досконалість легованих кристалів, одержано криві дифракційного відбивання (КДВ) від площин росту (100) та (101). Виявлено дроблення КДВ, обумовлене утворенням макроступенів росту при блокуванні просування елементарних ступенів при входженні легувальної домішки. Ріст на площині (100) здійснюється з утворенням більших макроступенів росту, ніж на площині (101). Домішка Tl^+ переважно адсорбується на грані (100) кристала. Показано, що коефіцієнт розподілення домішки Tl^+ для площин (100) та (101) відрізняється вдвічі: відповідно 1,0 та 0,5. Домішка талію у межах концентрацій ($C_{Tl} \leq 1$ мас.%) не впливає істотно на структурну досконалість легованих кристалів ADP.