Cryst. Res. Technol. **38**, No. 11, 941 – 945 (2003) / **DOI** 10.1002/crat.200310117

Study on rapid growth of highly-deuterated DKDP crystals

S. L. Wang *, Z. S. Gao, Y. J. Fu, A. D. Duan, X. Sun, C. S. Fang, X. Q. Wang

State Key Laboratory of Crystal Materials, Institute of Crystals, Shandong University, Jinan 250100, P. R. China

Received 16 January 2003, revised 3 April 2003, accepted 15 June 2003
Published online 15 October 2003

Key words DKDP crystals, rapid growth, solubility transition, growth rate.
PACS 81. 10. Dn

Highly-deuterated potassium dihydrogen phosphate (DKDP) crystals were grown rapidly from point seeds under high supersaturation in a temperature range of 40-60 ºC. The growth rate was about 1-2 order of magnitude higher than that of the traditional temperature reduction method. It was found that highly pure raw materials, overheating at high temperature, ultrafine filtration and supersaturation stability were needed to keep the solution from spontaneous nucleation at high overcooling. The effect of growth conditions on pyramid faces was different from that of prismatic faces. The tetragonal to monoclinic phase solubility transition scarcely occurred in our experiments even though the overcooling of monoclinic phase was as high as 10 °C in some cases.

1 Introduction

Tetragonal $K(D_XH_{1-X})_2PO_4$ (DKDP) crystal is a deuterated analog of KH_2PO_4 (KDP) crystal. Large and perfect tetragonal DKDP single crystals with high deuterium concentration are required in solid-state light valve, light deflectors and laser communication devices for easier operation [1]. Also in large-aperture fusion laser, DKDP was used as frequency converter such as doubler and tripler to avoid laser damage caused by stimulated Raman scattering (SRS), which may occur in KDP crystals [2].

Due to isotope effect, DKDP crystal may exist in two polymorphs, the tetragonal form (point group 42m) and monoclinic form (point group 2). The polymorphism of DKDP crystal gives some difficulties in the growth of the tetragonal crystal. The tetragonal-monoclinic phase transition temperature decreases with the rise of deuterium concentration in the crystal, which depends on that of the solution in which the crystal grows. The phase equilibrium transition point of 99.6mol% deuterated solution is 21±0.5ºC while that of 90mol% deuterated solution is 49±1ºC. Thus the degree of deuteration of DKDP has imposed strict temperature limits to the growth process. For example, tetragonal DKDP can be just grown traditionally from a starting temperature as high as 43ºC from a solution of 99.3% deuterium concentration by temperature lowing method [3]. For the growth of large highly deuterated crystal by cooling technique, a high starting temperature is needed in order to get a large temperature interval for cooling. In the present study, highly deuterated DKDP crystals were grown rapidly from a high starting temperature near 60ºC using a new developed point-seed technique [4]. The effect of growth conditions such as pD value, supersaturation, impurities and concentrations of growth solution on pyramid and prismatic faces was studied.

2 Experimental

There were three kinds of growth solutions. The first is synthesized by using the usual procedure. Commercial phosphorus pentoxide (P_2O_5) reagent of spec-pure grade (purity of 99.999%) were used to react with heavy

* Corresponding author: e-mail: slwang@icm.sdu.edu.cn

water of isotopic purity 99.9%, then the ortho-phosphoric acid obtained was reacted with AR grade potassium carbonate (K_2CO_3). The reactions are as follows:

$$P_2O_5+3D_2O \rightarrow 2D_3PO_4 \tag{1}$$

$$2D_3PO_4+K_2CO_3+D_2O \rightarrow 2KD_2PO_4+2D_2O+CO_2\uparrow \tag{2}$$

To avoid deuterium loss, K_2CO_3 was baked at 100ºC before the reactions. The PD value of solution can be adjusted by the amount of K_2CO_3. The deuterium concentration of solution can be decreased by adding double-stilled water.

The other two kinds of solutions were prepared by dissolving two kinds of KDP raw materials in heavy water. One KDP raw material is of commercial AR grade. The other is spec-pure grade KDP raw material having low concentrations of Cr^{3+}, Fe^{3+}, Al^{3+} (<1ppm)

Highly deuterated potassium dihydrogen phosphate (DKDP) crystals were grown rapidly from a 5l Holden-type crystallizer with temperature control±0.02ºC. All crystals were grown from approximate 8×8mm^2 z-cut point seeds under high supersaturation within a temperature range of 40-60ºC. The rotation mode of forward-stop-backward was adopted with a speed about 80 rpm. The crystals grew upwards.

3 Results and discussion

3.1 Stability of supersaturated solution

Before crystallization, the solutions were filtered through a 0.1µm membrane to remove extraneous solid and colloidal particles, which may act as the centers of spontaneous nucleation during growth. These particles can also be incorporated into the crystals during growth and deteriorate their optical quality. To prevent second contamination from the dust in air, the filtration was done under slight over pressure in a closed system. After filtration the solutions were overheated at 80ºC for 24h. This duration of overheating was found to be effective to destroy the molecule clusters existing in the solution and to make the solution stable against spontaneous nucleation under a high supersaturation [4, 5]. To avoid opening the crystallizer, a specially designed protector was used to prevent the seeds from dissolving when the solution was overheated.

The mismatch between the seed and the crystal grown onto it will break the stability of highly supersaturated solution. The deuterium concentration of the seed crystal should be consistent with that of the crystal prepared directed from the growth solution. If the seed does not match with the growth solution in the deuterium concentration, tiny tetragonal DKDP crystals can be observed in the bottom of the growth vessel just after regeneration of the seed. This phenomenon indicates that the stability of the supersaturated solution is broken up by the secondary nucleation induced by cracking of the growing seed crystal during regeneration [6]. When the seeds crystal were prepared from the mother liquor to be used, a high supersaturation was maintained without spontaneous nucleation, and the crystals were grown at rates about 1-2 order of magnitude higher than that applied in the traditional temperature reduction method.

3.2 Crystal transition

In our tests, perfect tetragonal DKDP crystals without inclusions, crack and milky regions just like those produced by traditional slow cooling technique can be grown rapidly from a high starting temperature without parasitic monoclinic crystals after ultrafine filtration and overheating. For example, tetragonal crystal C-1 was grown from a solution of 99.5mol% deuteration at a starting temperature of 60.5ºC, which is much higher than the starting temperature 43ºC used in the traditional slow cooling technique [3]. This improvement of starting temperature is of great significance for the growth of large highly deuterated crystals. It's much easy for N. P. Zaitseva et al [7] to start routine DKDP growth at about 73ºC from a solution of 90mol% deuteration because DKDP crystals can be grown from a solution of 89.8mol% deuteration at a starting temperature around 70ºC by traditional slow cooling technique according to Jiang Minhua et al [3]. The growth rate of C-1 was

36mm/day in [001] direction and 30mm/day in [100] direction, while that by traditional way is less than 1mm/day in [001] direction and near to zero in [100] direction. Our tests show that a larger cooling interval needed to grow larger deuterated crystals can be obtained in rapid growth technique.

The tetragonal to monoclinic phase solubility transition in solutions scarcely occurred in our experiments even though the overcooling of monoclinic phase was as high as 10ºC in some cases. Our experience of rapid growth indicated that this transition may occur when the tetragonal crystal is grown from the solution of 99.5mol% deuteration at a starting temperature higher than 60ºC. This transition always began from the seeds in our experiments when it happened. As a result of the transition, the crystals were cracked and the monoclinic crystals would eat away the tetragonal parent crystal in the end. This phenomenon indicated that the perfection and cleaning of seeds crystal maybe have something to do with crystal transition. Especially, large amount of imperfections are produced during the regeneration of seed crystal. These imperfections locally having a higher energy are easy to become the starting point of phase transition.

3.1 Effect of supersaturation, acidity, impurities and temperature on growth rate

Supersaturation, acidity, impurity and temperature are the main factors influencing the growth of tetragonal DKDP crystals. The effect of these growth conditions on pyramid faces was different from that on prismatic faces, as is shown in Table 1. Obviously, supersaturation is the most important parameter to rapid growth of crystals. The higher supersaturatiion, the faster the crystal grows. At medium supersaturation, the growth rate of prismatic faces increases stronger with increasing overcooling than that of pyramid faces. Accordingly, crystal habits change with the overcooling of solution during growth. The rate Lx/Hz (length rate of x and z direction of crystal) can show the tendency of shape modification. Lx/Hz increases with higher overcooling. We think this phenomenon can attribute to that the supersaturation is between σ^* and linear region where the step velocity on prismatic faces rises rapidly with supersaturation while the growth rates of pyramidal faces have a linear dependency on supersaturation [8]. As the supersaturation enters the linear region, Lx/Hz tends to a constant.

The acidity shows no effect on prismatic faces while the growth rate of pyramid faces decreases greatly with the deviation of pD value of solution from the intrinsic one. As the pD value is lowered from 4.2 to 3.1 and 2.3, the growth rate in [100] direction decreases from 31mm/day to 25 and 15mm/day, and Lx/Hz rises from 0.83 to 0.96 and 1.43 consequently. We ascribe this decrease of growth speed to a reduction of the concentration of $H_2PO_4^-$ ions in solution which is caused by lowering pD value. When the pD value of solution is lowered from 4.2 to 2.3, the concentration of $H_2PO_4^-$ is reduced to nearly 50% [9]. For pyramidal faces of DKDP are covered by K^+ in solution and electrostatic force is dominant one during growth, the adsorption of $H_2PO_4^-$ on growing faces predominate growth speed in z-direction [10]. On the other hand, prismatic faces are covered by K^+ and $H_2PO_4^-$ in parallel and electrostatic and H-bond cooperate in growth of (100) faces. As a result, growth rates decline significantly in z-direction and change little in x-direction with the drop of $H_2PO_4^-$ concentration when the pD value is lowered.

Table 1 Growth characteristics of some DKDP crystals.

Sample	Deuterium concentration	Saturation temperature	PD value	Super-cooling	Growth rate Rx/Rz(mm/day)	L_x/H_z
C-1	99.5	60.5ºC	4.1	6ºC	30/36	0.83
C-2	99.5%	57.2ºC	4.2	6ºC	25/31	0.83
C-3	99.5%	57.7ºC	4.3	7ºC	32/36	0.89
C-4	99.5%	58.1ºC	4.3	8ºC	40/40	1.04
C-6	99.5%	54.3ºC	4.3	6ºC	22/27	0.84
Ca-2	99.5%	57.0ºC	3.1	6ºC	24/23	0.96
Ca-5	99.5%	56.8ºC	2.3	6ºC	25/15	1.43
Cw-1	90.5%	57.6ºC	4.2	6ºC	25/30	0.85
HP-2	90.1%	58.3ºC	4.2	6ºC	24/30	0.82
AR-2	90.2%	57.8ºC	4.3	6ºC	18/31	0.67

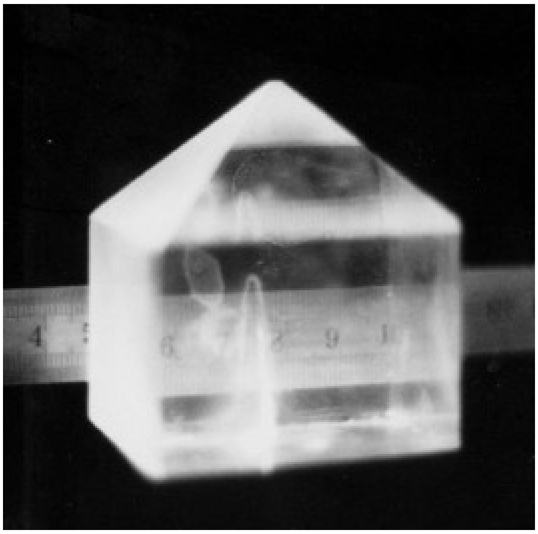

Fig 1 DKDP crystal C-2 has a size of 52×53×63mm³. The duration of the growth run was 40hour. The crystal looks blurred because it has been laid to open air for months. The milk zones were produced by condensed water before the crystal was taken from the crystallizer.

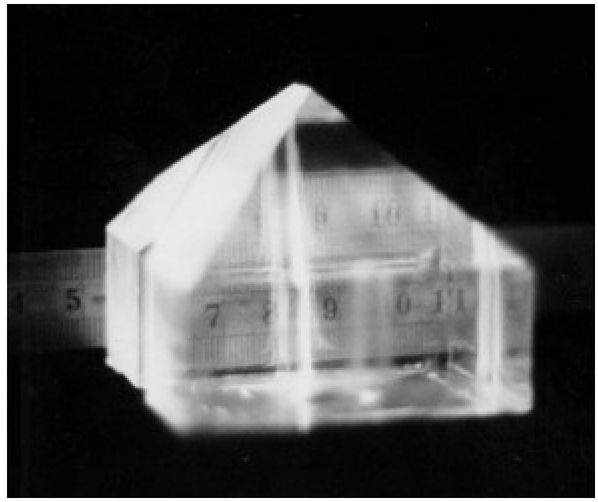

Fig 2 DKDP crystal C-4 has a size of 55×56×54mm³. The duration of the growth run was 27hour. The concaves in the middle of the prismatic faces were produced when crystal reached the pillar of seed holder during its growth.

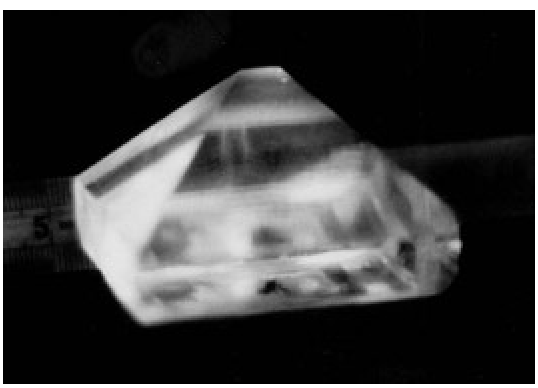

Fig 3 DKDP crystal Ca-5 has a size of 52×51×36mm³. The duration of the growth run was 40hour.

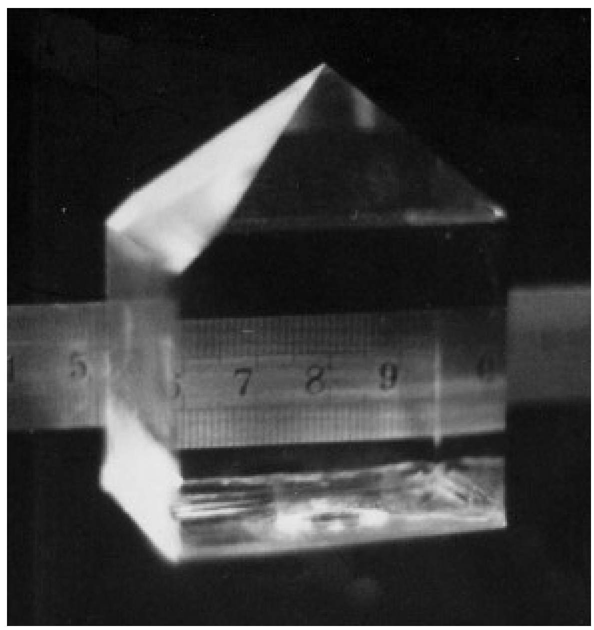

Fig 4 DKDP crystal has a size of 40×40×62mm³. The duration of the growth run was 40hour.

In contrast to acidity, the high-valence metallic impurities such as Cr^{3+}, Fe^{3+} etc have a strong inhibitive effect on prismatic faces whereas its influence on pyramid faces is small. This effect can be seen from the crystals AR-1 and HP-1 grown from the solutions prepared by dissolving AR and Spec-pure KDP raw materials in heavy water. These solutions have a deuterium concentration near 90%. The concentration of Cr^{3+}, Fe^{3+} etc in AR KDP raw material is near 5ppm respectively, which is much higher in comparison with those in spec-pure KDP and synthesized DKDP materials. It is well-known that the existence of trivalent metal impurities in solution expands the dead zone of KDP-type crystals growth in x-direction [8]. As the result of the reduction in (100) growth rate, the ratio of Lx/Hz declines with the concentration increase of trivalent metal impurities in solution accordingly.

Temperature is also a dominant parameter affecting growth speed. At same overcoolings, the growth rates of both prismatic and pyramid faces increase with the rise of temperature. The effect of temperature on tetragonal DKDP growth rates agrees well to the kinetics of crystal growth. The growth speed R can be written as follows [11]

$$R=B\sigma^n \tag{3}$$

$$B=A\exp(-E/kT) \tag{4}$$

Here σ is supersaturation, n is the reaction grade on growing surface, B is the constant of growth rate, E is active energy, k is Boltzmann constant, T is temperature. From these equations, it's easy to understand that the crystal grows fast with the increase of supersaturation and temperature.

4 Conclusions

Highly-deuterated tetragonal DKDP crystals were grown at rate about 1-2 order of magnitude as that by traditional temperature reduction method from a starting temperature around 60°C. It was found that highly pure raw materials, overheating at high temperature, ultrafine filtration and supersaturation stability were needed to keep growing solution from spontaneous nucleation at high overcooling. In rapid growth technique, tetragonal-to-monoclinic solubility transition can be avoided and a larger temperature interval for cooling needed to grow larger deuterated crystal by cooling technique can be obtained. It can be concluded that higher temperature, greater supersaturation, less high-valence metal impurities and a pD value around 4.5 are helpful to improve the growth speed.

Acknowledgments This work is financially supported by the State High Technology Program for Inertial Confinement Fusion and Youth Foundation of Shandong university.

References

[1] J. C. Salvo, IEEE Trans. Electron Dev. **18**, 748 (1971).
[2] J. H. Campbell, L. J. Atherton, J. J. De Yoreo et al., ICF Quarterly Report 5(1), Lawrence Livermore National Laboratory, Livemore, CA, UCRL-LR-105821-95-1, 1(1995).
[3] M. H. Jiang, C. S. Fang, X. L. Yu et al., J. Cryst. Growth **53**, 283 (1981).
[4] N. P. Zaitseva, L. N. Rashkovich, S. V. Bogatyreeva, J. Cryst. Growth **148**, 276 (1995).
[5] M. Nakatsuka, K. Fujioka, T. Kanabe, H. Fujita, J. Cryst. Growth **171**, 531 (1997).
[6] A. Chernov, N. P. Zaitseva, and L. N. Rashkovich, J. Cryst. Growth **102**, 793 (1990).
[7] N. P. Zaitseva, J. Atherton, R. Rozsa et al., J. Cryst. Growth **197**, 911 (1999).
[8] T. A. Land, T. L. Matin, S. Potapenko, G. T. Palmore, and J. J. De Yoreo, Nature **399,** 442 (1999).
[9] W. S. Wang, Y. J. Cao, J. Nanjin University (Natural Science Edition, in chinese) **32**, 60 (1983).
[10] S. A. de Vries, E. Vlieg, P. Goedtkindt et al., Abstracts of 12th Intern. Conf. On Crystal Growth in conjunction with 10th Intern. Conf. On Vapor Growth and Expitaxy (Jerusalem, Israel), 143 (1998).
[11] K. C. Zhang, L. H. Zhang, Crystal growth science and technology, Science Press (in Chinese), 231 (1997).