

FINAL REPORT

GROWTH OF KH_2PO_4 CRYSTALS AT
CONSTANT TEMPERATURE AND SUPERSATURATION

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by

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SUMMARY

A large three-zone crystallizer system was constructed and successfully operated for growing KH_2PO_4 single crystals. Under conditions of constant crystallization temperature and supersaturation, growth rates exceeding 5 mm per day were demonstrated for KH_2PO_4 crystals of 5 x 5 cm cross section. The optical quality of these crystals was equivalent to that of crystals grown at rates presently considered as state-of-the-art (~ 1 mm/day). Sample crystals were supplied for comparison testing. The three-zone system appears to be ideally suitable for growth of large-diameter KH_2PO_4 crystals for the Laser Fusion Program.

TABLE OF CONTENTS

<u>Section</u>	<u>Page</u>
SUMMARY.....	iii
LIST OF FIGURES.....	vii
LIST OF TABLES.....	viii
1. INTRODUCTION.....	1
1.1 Background.....	1
1.2 Statement of Work.....	3
2. THEORETICAL ASPECTS OF CRYSTALLIZATION FROM SOLUTION.....	3
3. CRYSTALLIZER SYSTEM.....	6
4. CRYSTAL GROWTH EXPERIMENTS.....	11
4.1 Raw Materials.....	11
4.2 Seed Crystals.....	14
4.3 Crystal Growth Parameters.....	15
5. RESULTS AND DISCUSSION.....	17
5.1 General.....	17
5.2 Growth Rate Measurements.....	20
5.3 X-Y Growth.....	22
5.4 Maximum Growth Rate in KH_2PO_4	25
5.5 Crystal Quality.....	28
6. CONCLUSIONS.....	29
7. RECOMMENDATIONS.....	30
8. ACKNOWLEDGEMENTS.....	30
9. REFERENCES.....	31

Appendices

A	Possible Correlation of Laser Damage Threshold with Dislocation Density in KDP.....	A1
B	Bibliography of Solution Growth with Special Emphasis on KH_2PO_4 (Theoretical and Experimental).....	B1

LIST OF ILLUSTRATIONS

<u>Figure</u>	<u>Page</u>
1. Miers diagram for solubility/supersolubility.....	3
2. Maximum supersaturation vs. temperature for KH_2PO_4	6
3. Schematic of three-zone crystallizer.....	7
4. Photograph of three-zone crystallizer (top view).....	8
5. Photograph of three-zone crystallizer (side view).....	8
6. Flow meter calibration for KH_2PO_4 saturated at 35°C, pH 4.5... 10	10
7. Solubility of KH_2PO_4 in H_2O	13
8. Correlation of ΔT and ΔC for KH_2PO_4 at 35°C, pH 4.8.....	14
9. Temperature stability of crystallizer chamber at 35.00°C.....	16
10. Capping process in KH_2PO_4	18
11. Growth rate of KH_2PO_4 (PL-11).....	22
12. Average growth rates for KH_2PO_4 [001].....	26
13. Correlation of KH_2PO_4 growth rates with Mullins data.....	26
14. Maximum growth rates for KH_2PO_4	27

1. INTRODUCTION

1.1 Background

The crystal requirements for the NOVA laser system are presently beyond the state-of-the-art in solution crystal growth. If one considers the largest crystal needed (76 cm diameter) and evaluates the present state-of-growth technology, the goal appears unattainable. In addition, the concept of using segmented crystals in a four-unit configuration will reduce the maximum crystal diameter required from 76 cm down to about 40 cm. However, the technology required to produce even this reduced size is still not sufficiently developed.

The basic limitation in technology is associated with the general acceptance of those in the crystal business to use Holden-type crystallizers for growing crystals from solution. This limitation, however, is not based on scientific data, but can be attributed to a blind acceptance of historical procedures. The Holden-type crystallizer, initially reported in 1949, was the first unit which was considered suitable for production growth of large, single crystals (Refs. 1,2). During the past thirty years, numerous improvements and modifications of the original Holden crystallizer have been reported and used for the growth of both large and small crystals, in both research laboratories and production facilities (Refs. 3,4,5).

The basic process for crystal growth with a Holden crystallizer is simple. A saturated solution of the material to be grown is introduced into the crystallizer which contains a number of seed crystals. The temperature of the crystallizer is maintained slightly above ($\sim 5^\circ\text{C}$) the saturation temperature of the growth solution. After the solution is transferred to the crystallizer, the temperature of the system is programmed down at a suitable rate. In some cases where the material to be grown has a retrograde solubility, the temperature is raised using a programmer. The two major problems with this type of process are: poor control over supersaturation, and a limit to the amount of solute available for growth. The first problem is discussed in the next section. The second problem can be appreciated if one considers that the amount of solution required to produce a KH_2PO_4 crystal of 76 cm cross-section exceeds 40,000 liters. This represents the volume of the growth chamber only, and the complete

crystallizer system would exceed 80,000 liters. With this in mind, it should be noted that the bulk of solution-growth technology has been developed using growth volumes in the 10 to 100 liter range. Working with such large volumes results in serious crystallizer design problems and significant unknowns in the crystal growth process.

This report discusses the technical aspects of a new approach for growing large crystals suitable for NOVA. The approach is not limited to KH_2PO_4 growth, but is a universal technique which can be applied to other water soluble crystals. In fact, Buckley in 1951 commented that "it would appear that the constant temperature crystallizer is the most useful type of crystallizer devised up to the present time for the growth of large, nearly perfect crystals from solution" (Ref. 3).

The nature of the laser damage mechanism in KH_2PO_4 is not fully understood. A brief discussion of a possible connection between crystal dislocations, impurities, and laser damage is given in Appendix A.

1.2 Statement of Problem

The major problem in growing large crystals of KH_2PO_4 is that the growth rate, using Holden type crystallizers, is limited to about 1 mm/day along the [001]. This limitation is determined by the occurrence of crystalline defects (i.e., veils) which can be observed to form parallel to the (101) faces of the crystal. While, in most cases, these defects can be observed visually, the use of a laser scattering technique can easily and clearly detect gross concentrations of these defects. The defect is caused by a fluctuation in growth rate which is directly related to uncontrolled supersaturation. Therefore, the key factor in determining the maximum growth rate possible for any material is to control supersaturation.

The solution of this problem is based on the use of a special crystallizer which operates under constant-temperature conditions and thus constant supersaturation. Based on published reports using small growth chambers, growth rates exceeding 5 mm/day can be obtained using this technique. The goal of our effort was to demonstrate that the maximum growth rate for KH_2PO_4 could exceed 5 mm/day without causing the normal types of defects usually observed.

2. THEORETICAL ASPECTS OF CRYSTALLIZATION FROM SOLUTION

The basis of all methods of solution crystal growth is illustrated by the Miers diagram shown in Figure 1 (Ref. 6). The solid curve (lower) represents the normal solubility curve for a solute/solvent system. The upper curve (dashed) is referred to as the supersolubility curve and denotes the temperature and concentration where spontaneous crystallization occurs. This curve is not well defined, and its position depends on a number of experimental parameters. However, for a fixed crystallization system, this curve position is fixed, and the distance between the two curves is called the metastable zone. It is within this zone that all crystal growth occurs.

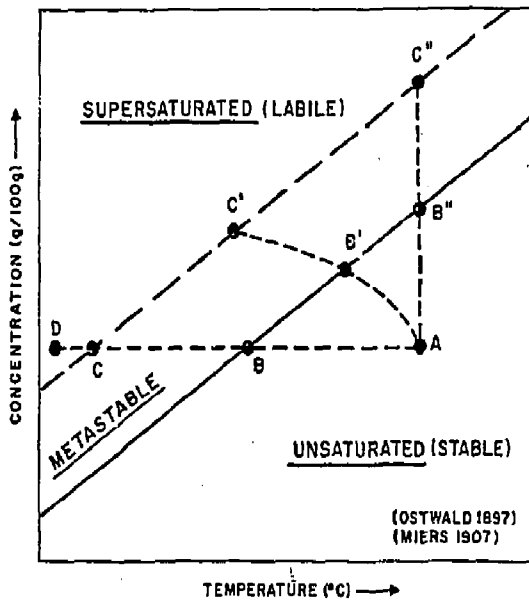


Figure 1. Miers diagram for solubility/supersolubility.

The diagram can be evaluated on the basis of three zones:

- The stable zone which is unsaturated and where crystal growth is not possible.
- The metastable zone where spontaneous crystallization is improbable but crystal growth on a seed occurs.
- The labile zone where spontaneous crystallization usually occurs.

When a solution represented by point A in Figure 1 is cooled without the loss of solvent, line AFG, spontaneous crystallization will occur only when conditions corresponding to point G are attained. Supersaturation can also be reached by isothermal evaporation (ABC), and, at point C, spontaneous crystallization is initiated. The line ADE illustrates the process where both cooling and evaporation occur simultaneously. It should be evident that controlled crystal growth on a seed is only possible within the metastable zone; thus, this region is of prime importance. The width of the metastable zone is identified as the supersaturation and must be specified in basic units of concentration. The most common expression of supersaturation is the concentration driving force ΔC , which is defined as,

$$\Delta C = C - C_0 \quad (1)$$

where, C = solute concentration in solution and C_0 = equilibrium saturation at a given temperature.

A second solution parameter which is useful is defined as the maximum or limiting supersaturation in a system. This is represented by the dashed line CFG in Figure 1. Synowiec, Nyvlt and Sohnel (Refs. 7,8,9) have expressed this parameter in the form of a simple expression,

$$\Delta C_{\max} = kMC_0 \quad (2)$$

where, ΔC_{\max} = limiting supersaturation, k = experimental constant, M = molecular weight of solute (g/mol), and C_0 = equilibrium saturation concentration. For dehydrated salts, the factor k in the temperature range 20-80°C is $0.855 \times 10^{-3} e^{-0.0163t}$, where t is the temperature in °C. Thus for a specific growth system, there is a limiting supersaturation, the width of the metastable zone can be determined, and these data can be used to develop the crystal growth process.

According to current solution growth theory, the growth rate of a crystal can be described as,

$$v_{hkl} = K\Delta C^n \quad (3)$$

where, v_{hkl} = growth rate in a particular crystallographic direction $\{hkl\}$, K = constant, and the exponent n varies from 1.4 to 1.6 (Ref. 5). It is also clear from current theory that the crystal growth rate can be linear at low supersaturations and at high supersaturation have a cubic dependence (Refs. 10-13). This could explain why current crystal growth rates are on the order of 1 mm/day for a wide range of different materials. The achievement of a high supersaturation which is highly desirable can not be obtained nor maintained in standard Holden-type crystallizers due to the lack of control over supersaturation. This results in the frequent occurrence of spontaneous nucleation. Therefore, an alternative method must be examined. The obvious choice would be a crystallizer which permits operation under conditions of constant temperature and supersaturation. Here, supersaturation is determined and maintained by a temperature difference (ΔT) between the saturating and crystallization chambers, and this ΔT is controlled at constant value.

The mathematics describing the growth rate of a crystal under conditions of constant supersaturation and temperature has been detailed by Kozlowski and Novotny (Refs. 14-15). Constant supersaturation is maintained by circulation of the growth solution at a constant rate. The major problem with this technique is spontaneous nucleation. However, if the width of the metastable zone is known, as described previously, the limiting supersaturation is never reached if ΔT is predetermined. In addition, a correct design of the crystallizer will eliminate spurious nucleation as it is generated.

The maximum values of ΔC , as a function of temperature, for KH_2PO_4 can be estimated by the technique described above (see Eq. 2). These results are given in Figure 2. From the data, the maximum ΔT which can be obtained in the KH_2PO_4 system is estimated by

$$\Delta C_{\max} = (dc^*/dT) \Delta T_{\max} \quad (4)$$

where (dc^*/dT) is the slope of the solubility curve in the temperature region of growth. For a temperature of 35°C in the crystallizer chamber, the maximum value of ΔT possible is 7.6°C.

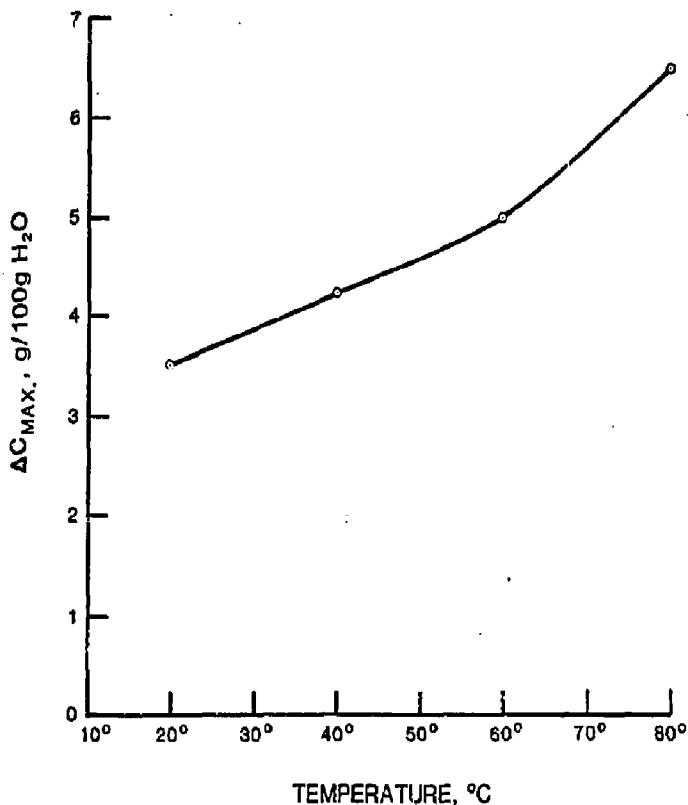


Figure 2. Maximum supersaturation vs. temperature for KH_2PO_4 .

A comprehensive literature search (see Appendix B) has revealed that crystal growth rates, from solution, exceeding 5 mm per day have been reported for numerous material, including KH_2PO_4 . However, the method of growth used to obtain these high rates was exclusively the constant temperature and supersaturation technique.

3. CRYSTALLIZER SYSTEM

Prior to the initiation of this program, the design of a three-zone crystallizer derived from the earlier version of Christensen and Walker (Ref. 16) was completed. The system consists of three chambers, viz, the crystallizer, superheat, and saturation, all of which are interconnected via heated tubes, thus forming a closed loop system. Figure 3 illustrates, schemati-

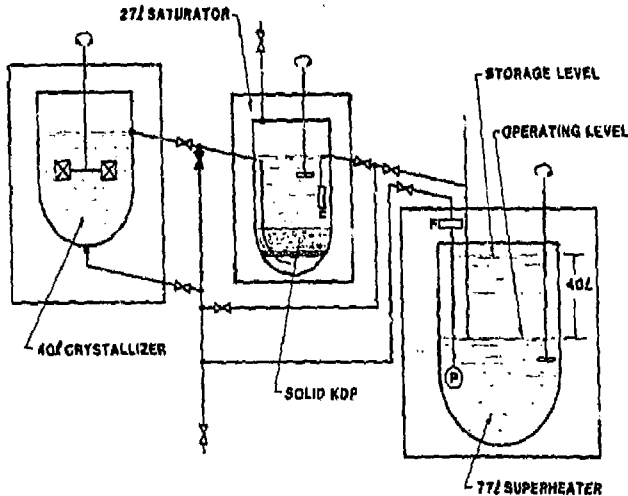


Figure 3. Schematic of three-zone crystallizer.

cally, the final system constructed for the program. Figures 4 and 5 are photographs of the operating system. The total internal volume of the system is 144 liters. The main differences between the previously described system and the new version are:

- All chambers are water-jacketed for thermal stability.
- The superheat chamber contains:
 - A 0.6 μm millipore filter.
 - Submersible Teflon gear pump.
 - Sufficient capacity to contain entire volume of the crystallizer chamber.
- Growth solution contacts only Teflon and glass surfaces.
- Temperature controllers capable of maintaining $\pm 0.001^\circ\text{C}$.
- Valve system to isolate each chamber.
- Saturator contains 100 μm glass filter.

The jackets for the main chambers were fabricated from commercially available stainless-steel tanks. These tanks were modified by welding-in dual observation ports and tube connections. The inner chambers which contain the growth solution were constructed from commercially available Pyrex jars. These jars were modified by our glassblower to permit the input



Figure 4. Photograph of three-zone crystallizer (top view).

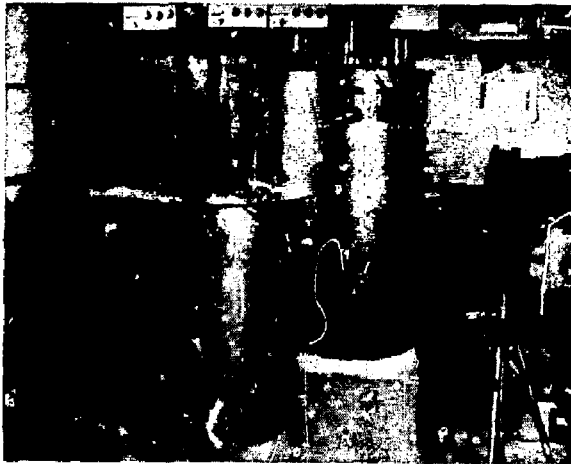


Figure 5. Photograph of three-zone crystallizer (side view).

tubes to enter the bottom of the jar and to exit from a side port. All connections are of Pyrex and/or Teflon. The lines and joints interconnecting the three system chambers are all made of Pyrex. A flexible Teflon joint was installed between the crystallizer and saturator chambers in order to give the line a degree of flexibility, thus avoiding potential breakage. The use of Pyrex and Teflon in this system completely eliminates the possibility of metallic contamination of the growth solution from the crystallizer.

The jacketed tanks are stirred by three motors (1500 rpm each). The crystallizer chamber has a fixed 10 rpm motor for rotating the seed tree. The saturator and superheat chambers are stirred by a 1500 rpm motor with a high-efficiency Teflon blade. The solution pump is powered by several fixed-speed motors. A minor problem was observed with the pump rate during the initial stages of the growth cycle. During the saturation period, a considerable amount of dirt accumulated on the millipore filter, thereby restricting the flow rate. To maintain a constant solution-flow rate, we found it necessary to replace the filter just prior to loading the solution and, subsequently, once again within 4 days after the run had started. This technique resulted in the maintenance of a flow rate (typically 4 liters/hr) to within ± 0.5 liter/hr.

The interconnecting lines were originally constructed of 3/8 inch diameter teflon tubing. However, the return lines from the crystallizer and saturator chambers are gravity fed and, due to surface-tension effects, solution flow had a tendency of stopping. To reduce this problem, the lines were changed to 1 inch diameter Teflon and glass tubing. This eliminated the flow stoppage, but additional problems of solution leakage at the Teflon-to-glass joints were observed. These joints could not be sealed using numerous techniques. The solution to this problem would be to replace all the interconnecting lines with a complete system of glass.

The solution flow was monitored by an in-line flowmeter constructed of glass and Teflon. The flowmeter is commercially available. Figure 6 illustrates the calibration curve of this flowmeter for a saturated (35°C) solution of KH_2PO_4 . The pH of the solution during calibration was 4.5.

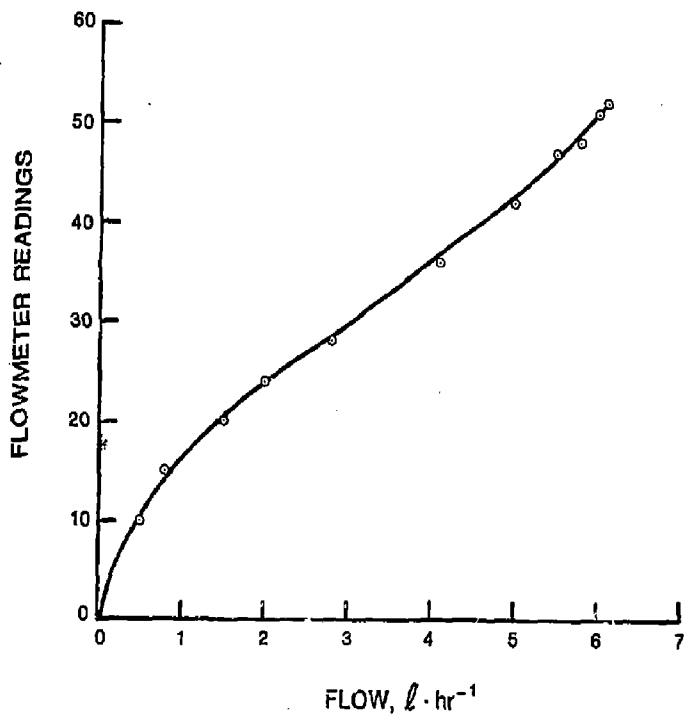


Figure 6. Flow meter calibration for KH_2PO_4 saturated at 35°C, pH 4.5.

4. CRYSTAL GROWTH EXPERIMENTS

4.1 Raw Materials

Three potential sources of KH_2PO_4 were investigated as starting material for these experiments. They were initially evaluated on the basis of purity, availability, and cost. Each candidate material was tested in a small-scale crystal growth run using a Holden type crystallizer. Table 1 summarizes the results of these experiments. Note that the pH values

TABLE 1. KH_2PO_4 Raw Materials.

	Ultrex ⁽¹⁾ L#74-9102 <u>Run #3-303</u>	MCB ⁽²⁾ PX1565 <u>Run #1-297</u>	MCB PX1566 <u>Run #3-301</u>
pH	4.82	4.62	4.91
Sat. Temp. (°C)	45.39	39.85	45.79
Volume (liters)	2	1.7	2
dT/dt (°C/day)	0.05→0.2	0.05→0.3	0.05→0.3
Seeds [mm (001)]	25 x 25	25 x 25	25 x 25
Taper angle (°)	11	9	0
ΔT, Total (°)	11.10	8.83	10.5
Fluid Vel. (cm/sec)	15	15	15
Yield (g/l/°C)	6.34	-	6.86

(1) Ultrex - J.T. Baker Chemical Co., N.J.

(2) MCB - MCB Manufacturing Chemists Inc., Ohio

listed are for the saturated solutions - without any adjustments (i.e., stoichiometric pH). The variation in pH is within the experimental error (+ 0.5) when concentrated solutions are used for measurements. Table 2 lists the impurity analysis of the three materials tested*. While the Ultrex material appears to contain very low levels of impurities associated with color and tapering in KH_2PO_4 , single crystals grown from this material were green and had an 11° taper. The MCB #PX1566 is a special low

* Analytical Lab., Ferroxcube Corp., N.Y.

TABLE 2. Impurity Analysis of KH_2PO_4 (concentrations, ppm).

<u>Element</u>	<u>Ultrex L#74-9102</u>	<u>MCB PX1565</u>	<u>MCB PX1566</u>
Al	< 1	-	< 5
Ba	< 2	-	< 5
Bi	< 5	-	< 5
Ca	0.7	< 100	< 10
Cd	< 0.4	-	< 10
Co	< 5	-	< 5
Cr	< 5	< 5	< 5
Cu	0.7	< 5	< 1
Fe	1	< 20	< 5
Mg	0.3	< 10	< 10
Mn	< 1	< 10	< 5
Na	18	< 100	< 50
Ni	< 5	-	< 5
Pb	< 10	< 10	< 5
Si	0.5	< 10	< 10

absorbance grade of KH_2PO_4 and our tests indicated that this material had less color than the Ultrex and 0° taper. The other MCB material is comparable to other ACS grade materials. All of these materials were grown in the same growth chamber under identical growth conditions; thus we feel that MCB #PX1566 is the best raw material for growth. In addition, the cost is about an order of magnitude less than that of Ultrex and only slightly higher than the standard purity.

Four solubility points were determined using MCB #PX1566 saturated solutions (pH 4.9); the data are given in Figure 7. The agreement with published values is excellent. This data was then used to establish the correlation between the temperature difference of the crystallizer and saturation chambers (ΔT_1) and the supersaturation for the three-zone crystallizer experiments. The bulk supersaturation in the crystallizer chamber is given by:

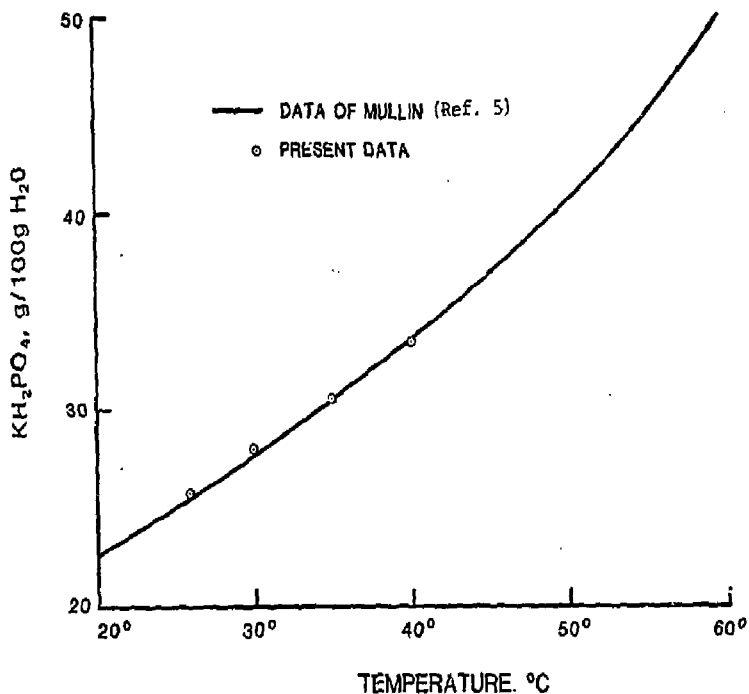


Figure 7. Solubility of KH_2PO_4 in H_2O .

$$\Delta C = C_{\circ T_1} - C_{\circ T_2} / C_{\circ T_2} \quad (5)$$

where, $C_{\circ T_1}$ = saturation concentration at temperature T_1 of saturator chamber.

$C_{\circ T_2}$ = saturation concentration at temperature T_2 of crystallizer chamber.

Using the data from Figure 7 and Equation (5), the relationship between the temperature differential of the saturator and crystallizer chambers and the actual supersaturation was calculated. The result is shown in Figure 8. With this data and the value of ΔC_{max} from Figure 2 for 35°C operation, it appears that the upper limit of ΔT is about 7°C.

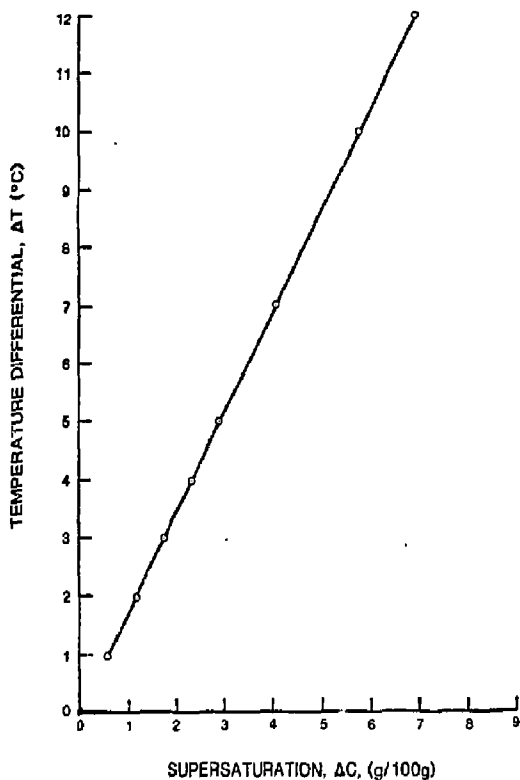


Figure 8. Correlation of ΔT and ΔC for KH_2PO_4 at $35^{\circ}C$, pH 4.8.

4.2 Seed Crystals

Ten seed crystals, 50x50x10 mm (0.2) plates, were purchased from Lasermetrics. Prior to loading, the plates were water polished and beveled on one edge to facilitate mounting. Initially the seeds were glued in place using Lucite holders previously reported (Ref. 17). Seed plates for subsequent experiments were fabricated from the previously grown boules. In one experiment (PL-15), seed plates of 127 x 127 mm were used to examine size effects on growth rate.

4.3 Crystal Growth Parameters

For the initial experiments, the following growth parameters were held constant:

- Solution flow rate: 4 ± 0.5 liters/hr
- Solution velocity: 15 cm/sec
- Seeds: 0%Z plates
- Filters: Saturation, 100 μ m
Superheater, 0.6 μ m
- Rotation sequence: 23 sec CW; 6 sec delay;
25 sec CCW; 7 sec delay

Three parameters were varied in these experiments: pH, supersaturation, and growth temperature.

The initial loading sequence was determined empirically. Several attempts to load the crystallizer with a large initial supersaturation resulted in spurious nucleation. The procedure developed requires the temperature differential between the crystallizer and saturator to be less than 0.1°C, and the differential between the crystallizer and superheat to be greater than 5°C. The time required for loading was fixed by the pump rate, which is regulated by the rpm of the pump motor. The crystallizer was typically loaded in four hours using a pump rate of 10 liters/hr. The temperature differential between the crystallizer and saturation chambers was then adjusted to the desired supersaturation level by increasing the temperature of the saturator. Concurrent within this operation, the temperature of the superheat chamber was raised to establish a differential of 10 to 15°C with the crystallizer chamber. Thermal equilibrium was established within 24 hours. The temperature of the transfer tubing was usually adjusted to coincide with the temperature of the superheat chamber.

Initial saturation of the growth solution (100 liter) required nearly seven days. The equilibrium at saturation was determined by: sampling the solution over a seven-day period, measuring the pH, and gravimetrically determining the total dissolved solids.

The total growth along the [001] was measured by photographing the entire crystal, at fixed magnification, on a daily basis. These pictures were

then analyzed and by use of a known dimension (seed holder thickness), the growth in mm was calculated. We estimate that the accuracy of these measurements is at least good to ± 0.1 mm.

The temperature stability of the crystallizer chamber was measured and continuously monitored for both short and long term stability. Figure 9 is a reproduction of the stability over a period of 10 hours. The short term stability is better than $\pm 0.001^\circ\text{C}$, while the longer term drift did not exceed $\pm 0.005^\circ\text{C}$ over a seven day period. The temperature control and stability in this system exceeds what is normally observed in a Holden type (temperature lowering) crystallizer. Note that the recorded temperature is that of the jacketed bath; the temperature of the growth chamber is expected to be at least a factor of two more stable.

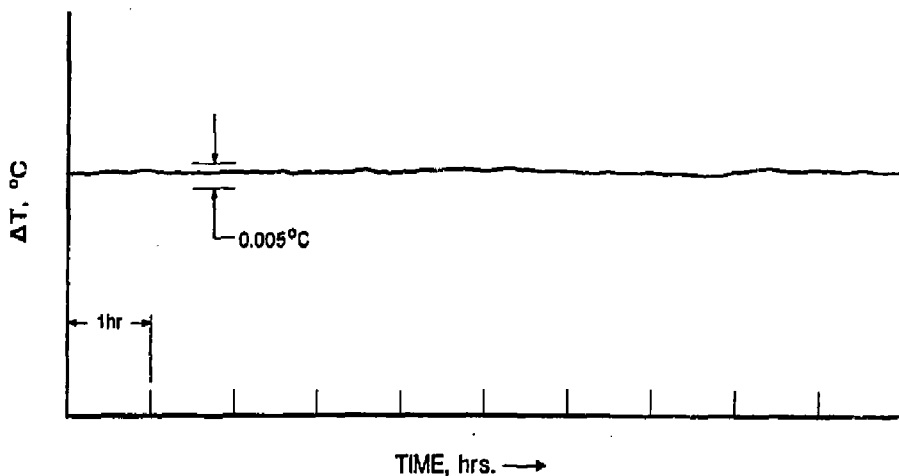


Figure 9. Temperature stability of crystallizer chamber at 35.00°C .

5. RESULTS AND DISCUSSIONS

5.1 General

A total of ten growth experiments were made with the new crystallizer system. The main objectives of the experiments were to establish the feasibility of a 5 mm/day growth rate for optical quality KH_2PO_4 and to gain experience with the system. Both goals were achieved.

The initial growth of KH_2PO_4 from a (001) plate is called the "capping process". This involves development of the [101] type facets and is characterized by a period of rapid growth accompanied by solvent inclusions. The process is illustrated in Figure 10. The first indication that growth has started is the appearance of a frosting over the seed plates - as shown at the top of Figure 10. The [101] facets then proceed to develop as shown, finally resulting in a completed cap. At this point, clear, unflawed growth is observed and growth-rate measurements for the [001] and [101] orientations can be obtained via the photographic process described in Section 4.3.

The total time required to establish the cap on a KH_2PO_4 seed plate varied from 2 to 12 days, depending mainly on the supersaturation value. This should be compared with a typical capping time from four to eight weeks for 5 x 5 cm seed plates grown by temperature lowering in a Holden-type system.

The results of the growth experiments are summarized in Table 3. The first run (PL-10) was aborted when the seed crystals fell out of their holder due to excessive dissolution. This was a direct result of attempting to load the crystallizer before the saturator had reached equilibrium. It was subsequently determined that a minimum of seven days was required to reach equilibrium when saturating a new solution.

Experiment PL-17 was terminated in 2 days due to complete blockage of the flow tubes.

Two crystal growth runs, PL-17 and PL-18, were made using seeds in the form of completed caps.

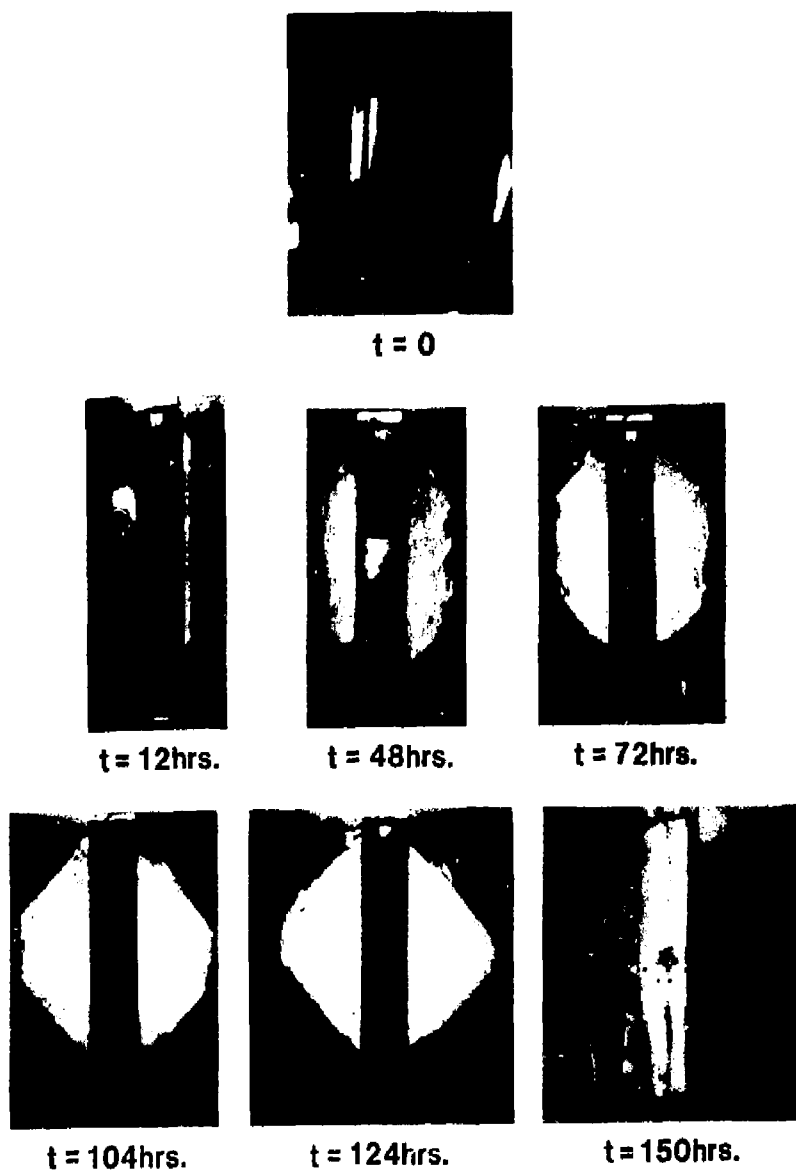


Figure 10. Capping process in KH_2PO_4 .

TABLE 3. Summary of KH_2PO_4 Crystal Growth Experiments.

Run No.	pH @ 22°C	Pump Flow Rate (liter·hr ⁻¹)	Solution Velocity V_1 (cm·sec ⁻¹)	Capping Time (Days @ ΔT , °C)	Growth Temperature (°C)	Super-saturation (ΔT_0 , °C)	Superheat (ΔT_1 , °C)	Average Growth Rate [001] ₁ (mm·day ⁻¹)
PL-10	4.8	-	-	-	-	-	-	-
PL-11	4.8	2.1-4.7	31	12 @ 1.0°	29.0	1.0-4.0	1.6-4.2	0.8-1.6
PL-12	3.6	0.5-6.2	31	5 @ 2.1°	30.5	0.5-5.1	2.1-7.1	0.8-3.2
PL-13	3.8	1.0-2.3	31	3 @ 1.9°	35.7	1.9-5.2	1.1-4.3	1.7-6.3
PL-14	2.9	4.1-6.1	31	2 @ 1.9°	35.1	0.04-1.9	2.9-11.7	1.6-4.2
PL-15	3.1	3.8-6.2	24	8 @ 1.8°	36.1	0.9-1.8	9.8	2.3
PL-16	2.6	3.0-4.7	31	3 @ 4.8°	34.1	2.0-4.8	14.6-19.2	4.1-5.5
PL-17	2.6	6.5	24	-	35.1	1.0	-	-
PL-18	2.2	4.8	24	-	35.1	3.1-4.0	2.2-13.6	0.9-3.4
PL-19	2.0	3.5-4.2	4-24-93	3 @ 1.4°	35.1	1.4	3.8-14.9	1.2-5.2

Run PL-15 used a seed plate 161.3 cm^2 in cross section. The results show that increasing the size of the seed plate from 25 cm^2 had no observable effect on growth rate, in comparison with other runs at similar growth conditions.

5.2 Growth Rate Measurements

The measurement of growth rate in these experiments was direct and relatively accurate. However, interpretation and analysis was complicated by several factors. First, it became evident that the acquisition of data was too fast, thus equilibrium was never attained before the supersaturation level was adjusted to a new value. A simple analysis of the total system volume and solution flow rate showed that a minimum of 50 hours was required to completely equilibrate the growth solution after a temperature change - assuming perfect mixing in the various system chambers. It was experimentally determined that growth rate equilibrium was achieved in 140 to 160 hours by analyzing the data from PL-14 and PL-19.

Another problem in defining a growth rate value was the observation (in many cases) that opposite ends of the same boule were growing at significantly different rates. In addition, the measurements of $[101]$ growth (four measurements per boule, also demonstrated significant variations. Table 4 summarizes the raw data on run PL-11. The growth rates in the three orientations were calculated from these data and are listed in Table 5 and illustrated in Figure 11. It is apparent that the growth rate for a particular crystallographic direction is not constant. One possible cause of these fluctuations in growth rate could be attributed to a nonuniform level of supersaturation in the region of crystal growth. This could arise from insufficient mixing of the growth solution due to both inadequate solution velocity across the growing crystal surface and a low solution flow rate. Partial confirmation of this assumption was obtained in run PL-19. Under a set of constant growth conditions, the solution velocity was varied from 4 to 93 cm sec^{-1} , and the results indicated an improvement in crystal quality and a constant growth rate. Further work is needed to completely understand and thus develop a procedure for controlling this behavior.

TABLE 4. Total Growth of KH_2PO_4 (PL-11) [mm (+ 0.01)].*

Date, Time	Orientation	Total Growth Seed #1		Total Growth Seed #2	
		Left	Right	Left	Right
20 Apr, 0900	[001]	2.54	2.54	2.12	2.86
	[101]	7.11	5.69	5.08	6.46
	[110]	7.11	5.08	5.82	5.50
30 Apr, 0930	[001]	3.56	4.06	3.10	3.61
	[101]	8.13	6.60	6.19	7.85
	[110]	8.13	6.50	6.71	8.16
1 May, 0930	[001]	4.76	4.23	4.72	4.93
	[101]	9.53	7.51	7.56	8.92
	[110]	10.58	7.30	7.87	8.40
4 May, 0930	[001]	9.57	8.97	9.50	9.70
	[101]	13.10	11.09	9.60	11.00
	[110]	12.80	8.06	10.60	11.20
5 May, 0930	[001]	11.02	10.18	10.33	11.25
	[101]	13.12	11.65	10.33	11.46
	[110]	12.88	8.40	11.67	12.39

* $\Delta T = 2.0^\circ$, pH 4.8, $T_G = 29^\circ\text{C}$, $V = 15 \text{ cm sec}^{-1}$.

TABLE 5. Growth Rate of of KH_2PO_4 (PL-11) [$\text{mm}\cdot\text{day}^{-1}$].

Time (Hours)	Orientation	Growth Rate Seed #1		Growth Rate Seed #2	
		Left	Right	Left	Right
24	[001]	0.90	1.52	0.79	0.81
	[101]	0.00	0.57	0.37	0.32
	[110]	0.00	0.37	0.29	0.00
48	[001]	1.02	1.52	0.98	0.75
	[101]	1.02	0.91	1.11	1.39
	[110]	1.02	1.42	0.89	2.66
72	[001]	1.20	0.17	1.62	1.32
	[101]	1.40	0.91	1.37	1.07
	[110]	2.45	0.80	1.16	0.24
144	[001]	1.60	1.58	1.59	1.59
	[101]	1.19	1.19	0.68	0.69
	[110]	0.74	0.25	0.91	0.93
168	[001]	1.45	1.21	0.83	1.55
	[101]	0.02	0.56	0.73	0.46
	[110]	0.08	0.34	1.07	1.19

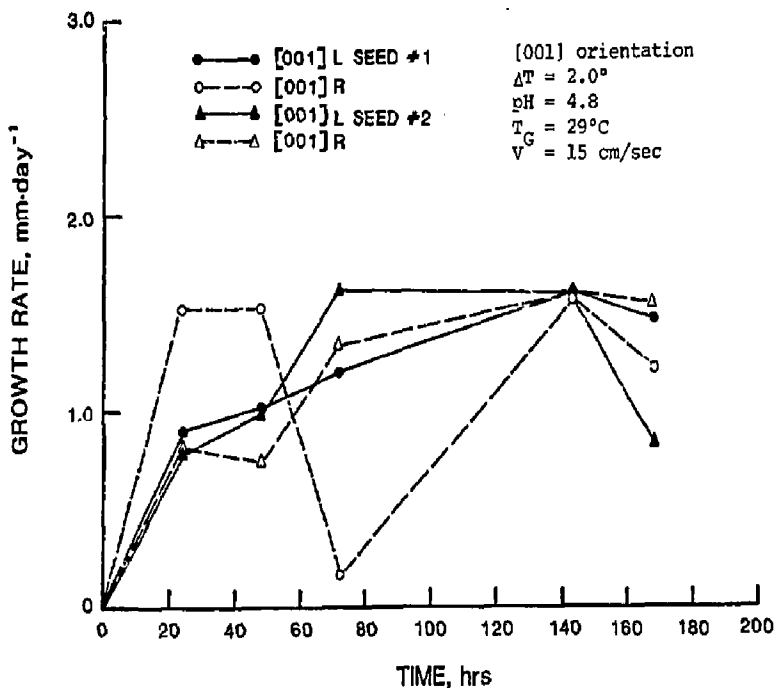


Figure 11. Crystal growth rate of KH_2PO_4 (PL-11).

In view of these difficulties, the crystal growth rates for the experiments were calculated by averaging the four [001] and eight [101] measurements.

5.3 X-Y Growth

There are numerous references in the literature regarding the effect of pH and impurity incorporation on X-Y growth in KH_2PO_4 (Refs. 3,5,18-23). The taper effect is also discussed in these references. While there is no clear consensus of opinion, the general conclusions can be summarized in two statements:

- The more acidic the growth solution pH, the less (essentially zero) growth in the X-Y directions.
- Taper is caused by the presence of impurities in the growth solution, typically Cr^{+3} , Fe^{+3} , etc. The green color observed is due to Cr^{+3} .

The results of our experiments have clearly demonstrated that the above statements above are not applicable to our growth conditions. We have observed X-Y growth over the entire pH range 2.0-4.9. This can be explained on the basis of Mullins, et al. work on KH_2PO_4 (Refs. 18,24). Using a standard solution of KH_2PO_4 at pH 4.7 (assumed), the growth rate as a function of supersaturation was shown to pass through three distinct regions of morphological changes. Over the region $\Delta C = 2-5$ g/100 g, the crystals tapered. In the region $\Delta C = 5-7$ g/100 g, the crystals had zero taper and above $\Delta C = 7$ g/100 g, X-Y growth was observed. Based on these results, it would appear that the dominant factor affecting both X-Y growth and taper is the supersaturation and not pH or impurities. Our data tentatively agrees with this conclusion. Table 6 list the ratio of {001}/[100] growth rates for our experiments together with the relevant growth parameters. There is clearly no dependency on pH. However, there appears to be a relationship between the maximum growth rate and the ratio of {001}/[100]. This suggests that as the rate of growth increases in the {001}, the rate in the [100] increases; thus the ratio approaches unity.

We also observed abnormal behavior of the green color effect in KH_2PO_4 . Table 7 summarizes these results. There is no correlation of colocation with pH as previously suggested by Mullin et al. (Refs. 5,24). In addition, the general assumption that color and taper are related has not been confirmed in these experiments. The green color usually observed in KH_2PO_4 has been attributed to the incorporation of Cr^{+3} in the form of a complex on the prism faces of KH_2PO_4 . In fact, Marecek, et al. reported that impurities such as Fe, Cr, Zn, Sn, Ni, Al, and Ca have no effect on taper at concentration levels of 1000 ppm (Ref. 25). Our results would tend to confirm their findings.

It is obvious that additional experiments with the three-zone crystallizer will result in a better understanding of the crystal growth process and could result in significant contributions to the theory of crystal growth from solution.

TABLE 6. Ratio of [001] to [100] Growth Rates in KH_2PO_4 .

Run No.	$V_{\text{max}}^{[001]}$ (mm/day)	V_{001}/V_{100}	pH	Growth Temp. (°C)	ΔT (°C)
PL-11	1.1	6.6	4.9	29	2
PL-12	3.2	4.3	4.0	30.5	4
PL-13	6.3	3.2	3.8	35.7	5
PL-14	3.3	2.5	2.9	35	1.9
PL-15	1.8	13.4	3.0	36.1	1.9
PL-16	5.5	6.0	2.6	34.1	4.8
PL-18	3.4	2.2	2.2	35.1	3.8
PL-19	2.8	6.2	2.0	35.1	1.4

TABLE 7. Presence of Color in KH_2PO_4 .

Run No.	pH	Remarks
PL-11	4.8	Two green bands adjacent to seed.
PL-12	3.6	Two very faint green bands.
PL-13	3.8	No color.
PL-14	2.9	No color.
PL-15	3.1	One strong green band.
PL-16	2.6	No color.
PL-17	2.6	No color.
PL-18	2.2	No color.
PL-19	2.0	Very faint green - no distinct bands.

5.4 Maximum Growth Rate in KH_2PO_4

The results of our experiments (Table 3) have clearly demonstrated that growth rates up to 6.3 mm/day can be obtained for KH_2PO_4 when growth occurs under the conditions of constant temperature and supersaturation. The maximum growth rate is defined as the rate where visible defects (flaws) are generated. The literature has numerous references to a critical growth rate and the assumption that "the larger the crystal, the slower the critical rate" (Refs. 26-29). However, in none of these references is a finite growth rate quoted. Thus, one may assume that the critical rate discussed could be 50 to 100 mm/day or larger.

References to "fast" rates of growth occur frequently in the literature. The first, for NH_4PO_4 , was given by Walker in 1947 (Ref. 30). In particular for KH_2PO_4 , growth rates as high as 16 to 35 mm/day are reported (Refs. 20,24), while typical rates of 5 to 10 mm/day are routinely cited (Refs. 11,21,31-34). From the results of this present study, it is clear that the maximum rate of growth for KH_2PO_4 has not been determined but is certainly above the 5 mm/day level.

One additional comment should be made with regard to the reported effect of crystal size on the critical growth rate. In 1915, Jones and Partington determined that larger seeds would result in a greater value of ΔC_{max} . Thus, if this theory of crystal growth is correct, this increase in ΔC will permit a higher rate of growth. We have observed that an increase in seed size from 25 to 161 cm^2 had no limiting effects on the maximum growth rate.

The average growth rates observed from runs PL-11 through PL-14 are shown in Figure 12. The growth rate dependency on supersaturation, or temperature differential ΔT , was compared with the data of Mullin, et al. (Ref. 24). The results, shown in Figure 13, indicate excellent agreement. The data of Mullin was recalculated in terms of mm per day at ΔT for a solution growth temperature averaged between 25° and 40°C. In terms of maximum growth rate as a function of temperature differential (i.e., supersaturation), Mullin's data was compared with the present work and the results are shown in Figure 14. Only three of Mullin's data points would fit this graph because at a ΔT of 6.5°C and growth temperature of 35°C,

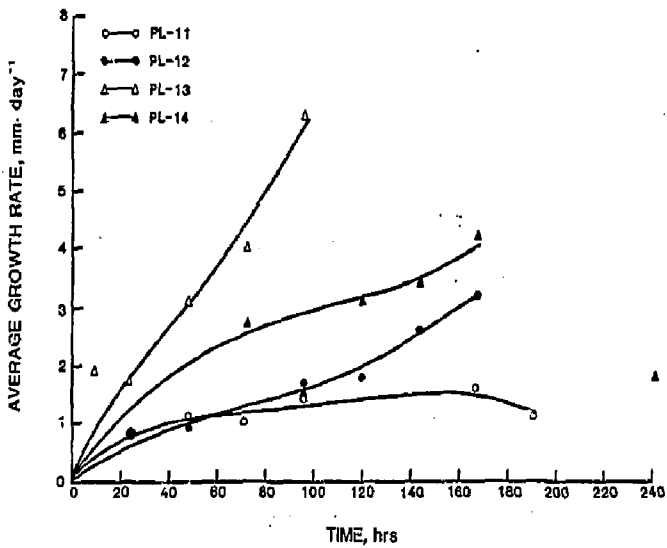


Figure 12. Average growth rates for KH_2PO_4 [001].

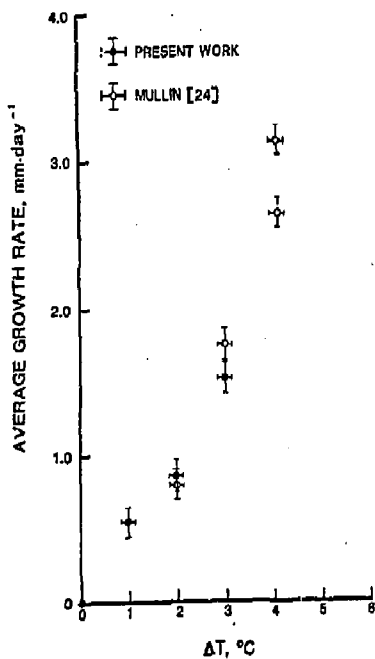


Figure 13. Correlation of KH_2PO_4 growth rates with Mullins data.

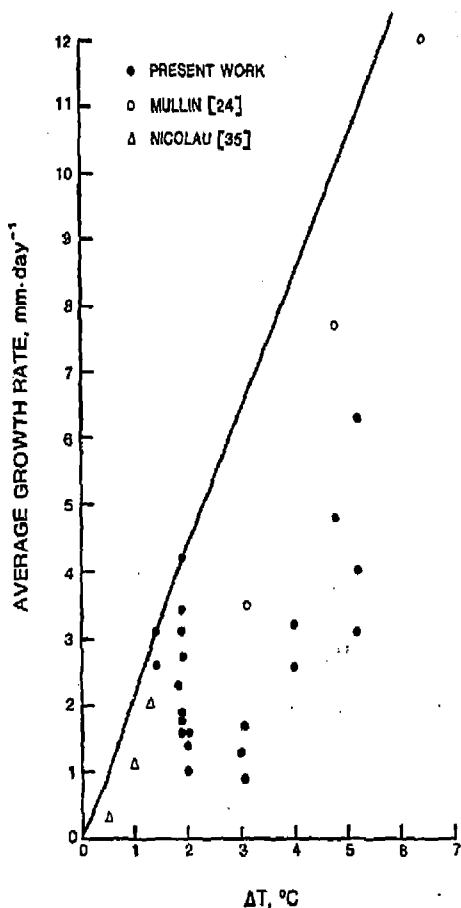


Figure 14. Maximum growth rates for KH_2PO_4

his rate was above 15 mm/day. He has no data points at $\Delta T = 2^\circ\text{C}$, claiming that growth was not observed in his system below a supersaturation of 2 g/100 g, which is equivalent to a $\Delta T = 3.2^\circ\text{C}$. We observed growth below this value as shown in the figure. The spread in growth-rate values between 0.7 to 3.5 mm/day at $\Delta T = 2^\circ\text{C}$ is indicative of the absence of equilibrium during the experiments. Dotted in the figure are values reported by Nicolau, which also agree well with the present work (Ref. 35).

A number of comments regarding the data presented in Figure 14 should be considered. The maximum values shown for $\Delta T = 1.4$ and 1.9° are true

equilibrium values. The three data points at $\Delta T = 5.2^\circ$ show that the growth rate was increasing, and the point at 6.3 mm/day is not a true maximum because the run was terminated due to flow problems in the system. Similar flow problems were encountered with the data points at $\Delta T = 3.1$ and 4°C . These facts must be considered and an assumption made that the maximum growth rate lies somewhere near the solid curve. The assumption should be examined in any future study.

5.5 Crystal Quality

The boules grown from these experiments were examined by a simple laser scattering technique using a He-Ne laser. In particular, scattering was sought in the [101] because the variation of growth rates may have caused inclusions or veils which were not visible to the eye. Without exception, all boules did not exhibit laser scattering by this technique. This indicates that the fast growth rates obtained did not affect the optical quality of KH_2PO_4 .

Two samples were supplied to Lawrence Livermore Laboratory for laser damage testing (Ref. 35). Single-shot threshold values of 8.4 and 8.1 J/cm^2 were measured. In addition, laser peak fluence of 15-16 J/cm^2 did not appear to increase the total number of damage sites as previously observed on commercially available KH_2PO_4 (Ref. 36).

The nature of the laser damage mechanism in KH_2PO_4 is presently under investigation at Lawrence Livermore Laboratory. A brief discussion of the possible connection between laser damage and dislocations is given in Appendix A.

In a separate effort, not covered by this program, Philips Laboratories has undertaken an x-ray topographic study of the crystals grown during this program. The objective is to determine the nature and extent of crystallographic defects in these crystals. The results of this investigation will be communicated at the completion of the study.

6. CONCLUSIONS

The results of this program clearly show that in a three-zone crystallizer, under conditions of constant supersaturation and growth temperature, growth rates in excess of 5 mm/day are possible for KH_2PO_4 . The maximum rate of growth lies somewhere above this value and, based on our data, could be assumed to lie in the 10-15 mm/day region. The three-zone crystallizer has been shown to be a superior apparatus for the growth of KH_2PO_4 .

Continuation of these studies will result in a significant contribution to the understanding of crystal-growth mechanisms and, therefore, could impact the theoretical aspects of crystal growth.

The growth of large crystals, 27 cm to 76 cm in diameter, is feasible in the three-zone system. A carefully engineered scale-up of the present system - with close attention to hydrodynamic properties of the apparatus - would be suitable for a pilot production facility. However, additional data is required - specifically the hydrodynamic properties of the system and their effect on growth rate - in order to insure proper operation.

It is conceivable that crystals up to 27 cm in diameter could be grown in the present system if a suitable method of seed holding could be developed. In particular, a method described by Belyustin and Stepanova would appear appropriate and should be investigated (Ref. 38).

The presence of X-Y growth, as observed under all of the experimental conditions investigated, could be a desirable aspect of growth via the three-zone system. The need to grow large cross-section seeds as the initial step in preparing large boules would be eliminated.

7. RECOMMENDATIONS

We recommend that this initial study be continued and the following tasks investigated:

- Determine maximum growth rate and maximum supersaturation level at 30, 40 and 50°C.
- Define effect of solution flow on growth rate.
- Determine hydrodynamic properties of system and their effects on growth rate.
- Develop a suitable seed-holder configuration to take advantage of the X-Y growth.
- Investigate growth of a large (15 x 15 to 27 x 27 cm) cross-section seed in the horizontal configuration.
- Compare of growth kinetics with present crystal-growth theory.

The evaluation of the above tasks together with the results of the present study will permit the design, construction and operation of a system suitable for growing the largest KH_2PO_4 crystals required for the Laser Fusion Program.

8. ACKNOWLEDGEMENTS

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TO: R. Bhargava

SUBJECT: Correlation of Laser Damage
Threshold with Dislocation
Density in KDP

FROM: G. M. Loiacono

In a recent paper, Endert and Melle [1] reported a direct correlation of laser damage threshold in KDP with dislocation density. KDP with a dislocation density of 10^3cm^{-2} had a threshold up to a factor of two lower than "perfect" regions of the crystal. Perfect crystals were defined as having dislocation densities of 2×10^2 to $6 \times 10^2 \text{cm}^{-2}$. There appears to be a threshold value where below $2 \times 10^2 \text{cm}^{-2}$ no significant increase in damage threshold was observed. While their studies were performed at 6900Å, these results can be reasonably extended to the 1.06µ region where LLL's present interest is to obtain highly damage resistant KDP for laser fusion applications.

The results of damage tests at LLL [2] has shown a wide variation in the threshold values for KDP - as supplied from three vendors. The reproducibility of thresholds in numerous KDP crystals supplied from the same vendor often varies by factors of 2 or 3. A preliminary evaluation of the possible correlation of damage threshold with a number of crystal growth parameters indicated no apparent correlation [3]. The same report also indicated no damage in crystals doped with impurities such as Cr and Fe up to concentrations of 4 and 17 ppm respectively. However, there is a published report by Endert and Martin [4] which shows a considerable reduction of damage threshold 2500 MW/cm² down to 320 MW/cm² when the Cr concentration changes from 90 to 0.9 ppm.

A number of x-ray topographic studies on KDP have clearly demonstrated the existence of impurities localized at dislocations [5,6]. In addition, the growth mechanism for KDP type crystals indicates that the principal growing faces [101] appear to be dislocation free [7]. If we now examine these factors, one can draw some reasonable conclusions that are relevant to a potential source of laser damage in KDP.

Impurities are known to segregate at growth interfaces and their distribution is strongly coupled to crystal growth parameters. In addition, dislocations are sites where impurities are known to precipitate. Thus the existence of dislocation bundles in extremely high density, would be expected to act as "gettering" locations for impurities present in the growth solution. The fact that dislocations have been observed, in high density and randomly distributed, in KDP crystals grown by the standard temperature lowering method, would lead one to conclude that if laser damage is associated with dislocations, then the damage would also be random. That is, the threshold values for damage would vary within the same crystal. This effect has been observed. Thus it is evident that low dislocation densities are desirable. If we now couple this with the observations that (a) [101] faces grow essentially dislocation free; (b) rapid capping of the pyramidal form of KDP - which is the generation of [101] faces - eliminates high dislocation densities present in the original

seeds and also eliminates those caused by solvent inclusions; (c) uniform crystal growth rates favor defect free crystals and finally (d) impurities are trapped at dislocations, it can be assumed that rapid capping is desirable in the growth process. We cap in two to five days using the three-zone method.

This may explain the fact that high damage threshold KDP is consistently grown by one vendor, who claims they cap KDP in about two weeks [8].

The laser damage results from LLL on our KDP crystals, grown by the three-zone method, show a threshold of 8.4 and 8.1 J/cm² for single shot tests [9]. In addition, higher energies and repeated shots do not generate the high damage site densities previously observed in all KDP samples obtained from growth by temperature lowering.

It is clear that growth by the three-zone method, in addition to the high growth rate advantage, may also be beneficial in terms of dislocation density reductions. To examine this assumption, we have convinced Bill Stacy that his expertise in x-ray topography is crucial to experiments and he has consented to examine a series of our samples. After Bill completes his study, we will submit these samples to Stan Stokowski at LLL for laser damage tests. Therefore, we hope to experimentally establish a correlation between damage threshold and dislocation density in KDP.



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APPENDIX B (Cont'd)

Supplement No. 1 to

Bibliography* of Solution Growth with Special Emphasis on KH_2PO_4
(Theoretical and Experimental)

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