Effect of crucible shape on the solution hydrodynamic in the growth of KTiOPO₄ single crystals by top-seeded solution growth method: A numerical analysis

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Three-dimensional solution flow and temperature field simulations were performed to model the growth of $KTiOPO_4$ single crystals by TSSG method. Steady flow and temperature field for four crucible shapes were computed using finite volume method. Our results show the effect of crucible shape on axial flow which has direct effect on homogeneity of solution, morphology of crystal and mass transport during the growth of crystals from solution. In order to consider the simulation results, $KTiOPO_4$ single crystals were grown by TSSG method in crucibles with different shapes.

Keywords: Top seeded solution growth, KTiOPO₄, Simulation, Crucible shape

1 Introduction

Potassium titanyl phosphate (KTiOPO₄ or KTP) is an excellent crystal for second-harmonic conversion of Nd-YAG laser radiation. KTP possesses several unique properties such as large non-linear optical (NLO) coefficient, wide acceptance angle, phase matching properties and high damage threshold¹. KTP melts incongruently² at 1172°C. Therefore, it is very difficult to grow the KTP crystals by conventional melt techniques. In order to obtain large single crystals, two main methods are commonly used, namely, the hydrothermal method³ and flux method^{4,5}. The hydrothermal method requires very sophisticated pressure equipment and has the disadvantages of incorporation of OH-ions which deteriorate the NLO properties. The alternative method is high temperature solution or flux method. Different types of fluxes have been used for the growth of KTP by flux method but within these fluxes, polyphosphate (K₆P₄O₁₃) has identified as a viable high temperature solvent for the growth⁶⁻⁸ of KTP.

However, grown crystals by flux method, have plagued by inclusions formation and spurious nucleation problems. The presence of solution inclusion flaws in a grown crystal which is the result of non-uniformities of the saturation field in the solution bulk, reduces the transparency of crystals, promotes undesirable strain throughout unflawed region and limits the volume of material suitable for device fabrication.

The effective parameters during the formation of inclusion in the growth of crystals from solution and inclusion formation mechanisms have been studied by many researchers. Bordui et al9. studied the effect of solution hydrodynamic on the inclusion formation during the growth of KTP crystals. They also established a preferred configuration for orientation and rotation of KTP crystals in K₆P₄O₁₃ flux by visual simulation. Vartak et $al^{10,11}$. simulated the growth system of Bordui by computer and studied supersaturation fields and steady flows in this system. But the effects of crucible shape on the solution hydrodynamic have been studied relatively few. Tavakoli *et al*¹². considered the effect of a flat and a rounded crucible bottom on the solution hydrodynamic in the growth of oxide crystals. Miyazawa *et al*¹³. have shown that the effect of tilt and shape of crucible on flow velocity and melt-crystal interface shape during the growth of multi-crystalline silicon by unidirectional solidification method.

In the present study, Navier-Stockse's continuity and energy equations have been solved numerically using finite volume method. The effect of crucible shape on the axial flow during the growth of crystals by TSSG method has been investigated. The temperature field and solution flow in the presence of free and forced convections have been studied. In order to consider the simulation results with experiments, KTP single crystals have been grown by TSSG method.

2 Theory

The physical model which is used in this analysis consists of a seed and crucibles with different shapes. Dimensions of crucibles are given in Table 1. In all these processes, seed is mounted directly to a support rod and rotating around z axis at the surface of solution. Pure glycerol was used as a liquid model. Physical properties of liquid are given in Table 2.

2.1 Governing Equations

Following assumptions have been made for solving energy and momentum equations:

- (1) Solution is an incompressible Newtonian fluid satisfying the Boussinesq approximation.
- (2) The system is in steady state condition.
- (3) The flow is laminar.

Thus, the fundamental equations are:

1 Continuity equation:

$$\nabla V = 0$$

2 Navier-Stokes equation with Boussinesq approximation:

$$V.\nabla V = -\frac{\nabla P}{\rho} + v\nabla^2 V + \beta g \Delta T \qquad \dots (2)$$

3 Energy equation:

$$\frac{\kappa}{\rho c_p} \nabla^2 T - V \cdot \nabla T = 0 \qquad \dots (3)$$

In Eqs (1-3), V is the velocity of solution, υ the kinematic viscosity, P the pressure, ρ the density, β is the thermal expansion coefficient of the solution, g is the earth's gravitational acceleration, ΔT is the

Table 1 — Dimensions of crucibles					
Type of crucible	R _{down} (mm)	R _{up} (mm)	$\alpha = R_{\rm down}/R_{\rm up}$ (mm)	H (mm)	
А	22.50	22.50	1.00	50	
В	19.87	22.50	0.88	50	
С	17.21	22.50	0.76	50	
D	13.76	22.50	0.61	50	
Table 2 — Physical properties of pure glycerol used for simulation					
Physical properties			Val	Value	
Kinematic viscosity (m^2/s)			0.520	0.520×10^{-3}	
Volumetric expansion coefficient (K^{-1})			¹) 4.84×	4.84×10^{-4}	
Specific heat (<i>j</i> /kg.K)			242	2427	
Thermal conductivity (w/m.K)			0.2	0.286	

temperature difference in solution, κ is the thermal conductivity coefficient and c_p is the specific heat.

Consistent with our assumption of steady-state condition, we apply no-slip boundary condition for the velocity field on the crystal and container wall, namely, at the solid-solution boundary:

V=0

...(1)

It is assumed that the air-solution interface to be flat and stationary. We put the heat flux constant on the container wall.

2.2 Numerical Method

The finite-volume scheme was used for discretizing the flow field equation. A segregated solver and an implicit technique were used to solve the algebraic equation formed from the discretization of the closed set of equations. SIMPLE algorithm was used for the calculation of the pressure and velocity field, which was needed for solving energy equation. Moreover, Hybrid grid scheme was used for grid generation (Fig. 1).

For the grid study of present simulation, four sets of grids were used. Considering the results with the maximum difference of average temperature at the center of domain with 0.85% difference, the case with 418240 nodes was used for the final simulation (Table 3).

3 Results and Discussion

The cylindrical shape of crucible and rotational motion of the seed suggest that it would be most useful to consider the velocity components in a cylindrical coordinate system: radial velocity (V_r) , azimuthal velocity (V_{θ}) , and axial velocity (V_z) . Flows in all of the simulations are driven by applied seed



Fig. 1 — Hybrid grid for domain meshing

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rotation in the counter-clockwise direction with the rotation rate of 60 rpm. The azimuthal velocities have higher magnitude than any other velocity component and they are zero at the container wall and reach a maximum of $r\omega$ along the outermost point of the spinning seed.

In the growth of crystals from high temperature solution, solution flow is a result of the interaction between flows caused by free and forced convections. Free convection caused by the difference in the density of solution layers which is the result of the change in temperature or concentration in the solution. On the other hand, forced convection which is the result of seed rotation, depends on many factors such as solution viscosity, diameter of crystal, the rate of seed rotation and density of solution.

Peshev *et al*¹⁴. have shown that in the presence of forced convection, solution tends to move up at the

Table 3 — Grid study data for crucible with α =1					
Case	Number of nodes	Average Temperature at center of domain (K)	Error Percent		
1	52600	301.07	0.85		
2	174960	302.60	0.34		
3	418240	303.65			
4	406308	304.00	0.14		

middle of crucible and moves down along the wall container. But with free convection, depending on the heating condition, there are two possible cases:

- 1 If the periphery of crucible is heated, solution tends to move up along the container wall and moves down at the middle of crucible.
- 2 If the bottom of crucible is heated, solution tends to move up at the middle of crucible and moves down along the container wall.

Consequently, the interaction of the forced convection flow with one or other kind of free convection will produce different resultant flow. Figure 2 shows the velocity vectors in the crucibles with 0.61< α <1. In the crucible with α =1 (Fig. 2a), forced convection plays more effective role than the free convection and solution tends to move towards the surface of crystal at the middle of crucible and move down along the container wall. So there is an axial flow under the crystal at the middle of crucible. In the crucible with α = 0.88, solution flow has same behaviour, but axial flow under the crystal in this shape is weaker than that of the crucible with α =1. By decreasing α , the temperature of solution in the lower part of crucibles increases while in the upper part of



Fig. 2 — Velocity vector in the crucibles with (a) $\alpha = 1$, (b) $\alpha = 0.88$, (c) $\alpha = 0.76$ and (d) $\alpha = 0.66$

crucibles decreases and the effect of natural convection becomes larger than forced convection (Fig. 3). Therefore, the axial flow under the crystal gradually becomes weaker and solution tends to have more rotation motion.

Axial flow is very important in the growth of crystals from solution and has direct effect on the homogeneity of solution, mass transfer and morphology of the grown crystals. Vartak *et al*¹⁰. have shown that when seed crystal is mounted perpendicular to Z axis, the axial flow causes mixing solution very well and supersaturation field in the solution becomes more uniform. On the other hand, according to first-order crystallization when a crystal is growing from solution, thin layers of solution near the crystal surfaces are solute-poor from the firstorder crystallization reaction occurring at the crystal surfaces, so for the continuing growth process, axial flows should move the solute-rich solution towards the surface of crystal from regions of higher bulk supersaturation.

In the crucible with α =1, because of axial flow, solution mixes very well and crystal grows uniformly. But in the crucibles with α =0.76 and α =0.66, the axial flow under crystal is very weak and solution has only rotation motion. So, in these shapes, solution does not mix very well and supersaturation field is non-uniform.

4 Experimental Details

The experiments were performed in a three-zone resistance heating furnace. Each zone was controlled separately with accuracy of $\pm 1^{\circ}$ C by Eurotherm controller. All the growth runs were performed with KPT/K₆ ratio of 0.6. The saturation temperature was measured at 943°C by testing seed crystal method. Platinum crucibles with same size but different shapes were used for the growth runs. Starting materials KH₂PO₄, TiO₂, HPO₄ (Merck Company) were weighed, mixed and sintered at furnace and temperature was raised to 1050°C and kept for 20 h.



Fig. 3 — Temperature field in the crucible with (a) $\alpha=1$, (b) $\alpha=0.88$, (c) $\alpha=0.76$ and (d) $\alpha=0.66$

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Fig. 4 — KTP single crystals are grown in the crucible with (a) α =0.75 and (b) α =0.95

When <001> oriented seeds were used, the maximum growth rate of the crystal would be downwards into the solution and larger size crystals could be obtained for device fabrication. Therefore, in the present study, <001> seed crystals with the dimension of $3 \times 4 \times 10 \text{ mm}^3$ were used in all of growth runs. Seed crystals mounted on alumina rod with platinum foil. Then, the seed rod was slowly lowered into furnace until the seed came in contact with the solution surface. The temperature of solution was maintained at 10°C above the saturation temperature to dissolve the outer surface of the seed. After about one hour, the temperature of solution was decreased to saturation temperature and growth was started at the cooling rate of 0.2°C/h. During the growth process, the seed was rotated with the speed of 60 rpm in counter clockwise direction. It took 17 days to complete each growth runs. After the growth was completed, the crystal was drawn out of the solution and furnace cooled down with the rate of 25°C/h.

5 Conclusions

Growth at the crystal facets is occurred via a firstorder crystallization reaction, which lowers the level of supersaturation at the crystal surfaces. While diffusion acts very near the crystal, convection is of paramount importance in the increasing of growth rate and homogenization of solution. Therefore, during the growth process, thin layers of solution near the crystal surface are solute-poor from the first-order crystallization reaction and axial flows move soluterich solution towards the surface of crystal from regions of higher bulk supersaturation. Figure 4 shows KTP single crystals grown in the crucibles with α =0.75 and α =0.95, respectively. Both the grown crystals are reddish-orange in colour due to incorporation of Rh impurities from crucibles. Since both the crystals have been grown under almost same experimental conditions, the difference in quality can be due to shape of the crucibles. In the crucible with α =0.95, about 25% of dissolved KTP precipitated on the seed and formed the as-grown KTP crystal but in the crucible with α =0.75, less than 20% of dissolved KTP precipitated on the seed. KTP precipitated on the seed. KTP crystal grown in crucible with α =0.95 looks more transparent and shows more complete faces as compared with KTP crystal grown in crucible with α =0.75.

Our results show that by decreasing the amount of α , axial flow in the crucible under the surface of crystal becomes weaker and the flow of solute-rich solution towards the surface of crystal is decreased. Therefore, the quality of grown crystal by decreasing the amount of α is reduced.

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