GROWTH OF LARGE SINGLE CRYSTALS OF KTiOPO\(_4\) (KTP) FROM HIGH-TEMPERATURE SOLUTION USING HEAT PIPE BASED FURNACE SYSTEM


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A process is reported for crystal growth of KTiOPO\(_4\) from its solution in K\(_6\)P\(_4\)O\(_{13}\) using a seeded, slow cooling technique. A new furnace system is reported for use in the process, its key feature being a heat pipe providing for a high degree of spatial temperature uniformity throughout the growth solution. Initial surface dissolution appears necessary to achieve flaw-free growth immediately off a seed. Avoidance of solution inclusion flawing in advanced stages of growth requires a crystal orientation configuration and rotation pattern that does not give rise to stable regions of uncirculating growth solution. Through the process, 10-day growth runs routinely produce flaw-free crystals large enough to yield plates 10 x 10 x 7 mm\(^3\) oriented in the optimal direction for second harmonic generation having properties measured to be at least as good as KTiOPO\(_4\) grown by other methods.

1. Introduction

KTiOPO\(_4\), commonly referred to as “KTP”, is recognized as possessing superior properties for use as a non-linear optical material [1–4]. Its widespread employment has been limited by a shortage of crystals of sufficient size and quality. Despite the application of a variety of crystal growth methods by a number of workers [5–15], the largest flaw-free volumes currently available commercially measure roughly 5 x 5 x 5 mm\(^3\) and are extremely costly [3].

Herein we present results of an extended study into the growth of KTiOPO\(_4\) crystals from high-temperature solution. Specifically, a process was developed for crystal growth of KTiOPO\(_4\) from its solution in K\(_6\)P\(_4\)O\(_{13}\) using a seeded, slow cooling technique. Through this process, 10-day growth runs routinely produce flaw-free crystals large enough to yield plates 10 x 10 x 7 mm\(^3\) oriented in the optimal direction for second harmonic generation having properties measured to be at least as good as KTiOPO\(_4\) grown by other methods.

2. Solution preparation and properties

Previous work [5,9] identified the liquid composition K\(_6\)P\(_4\)O\(_{13}\) as a viable high-temperature solvent for crystal growth of KTiOPO\(_4\). Notable advantages of this solvent composition are that it is relatively nonvolatile and that it contains no species foreign to KTiOPO\(_4\) itself. Liquid solutions of KTiOPO\(_4\) in K\(_6\)P\(_4\)O\(_{13}\) were made by in situ reaction of TiO\(_2\) (Aldrich, 99.9% pure), KH\(_2\)PO\(_4\) (MCB, A.C.S. Grade), and K\(_2\)HPO\(_4\) (Aldrich, ACS Grade) as previously described [9,16].

The solubility of KTiOPO\(_4\) in K\(_6\)P\(_4\)O\(_{13}\) over the temperature range of 900 to 1000°C is shown in fig. 1. These data were gathered over a large number of growth experiments and may be considered accurate within 1%. They represent a refinement of previously-reported data [9] over this narrower temperature range.

Measurements of the viscosity and density of KTiOPO\(_4\)/K\(_6\)P\(_4\)O\(_{13}\) crystal growth solutions were previously reported [16,17].

3. Furnace system

A new furnace system was designed and constructed specifically for the growth of KTiOPO\(_4\)
from its solution in $K_6P_4O_{13}$. A preliminary analysis of the kinetics of crystallization of KTiOPO$_4$ from $K_6P_4O_{13}$ indicated that the proposed process would be dominated by a combination of interface attachment and bulk mass transport resistance, and that the overall kinetic resistance to growth would be relatively large [16]. Such a situation is typical of many well-known processes of crystal growth from aqueous solution. To drive such a process at a rate viable for a production operation, it was seen necessary to provide for a significant level of bulk supersaturation in the region of the growing crystal. We felt a slow cooling technique would be the most reproducible and controllable method for achieving such a bulk supersaturation condition. In order to avoid copious spurious nucleation in the supersaturated solution during growth, it was in turn seen necessary to provide for a high degree of spatial temperature uniformity throughout the solution volume. Also, in light of the significant role to be played by mass transport and, therefore, fluid flow in the overall process, it was additionally seen necessary to incorporate some degree of flexibility into the designed approach to stirring the solution or moving the growing crystal through the solution.

The central component of the furnace system constructed following these design considerations is a vertically-oriented, resistance heated tube furnace, shown schematically in fig. 2. The key element in the furnace is a sodium-filled Inconel heat pipe which, lined with a protective silica glass tube, defines the furnace cavity. The highly efficient heat transfer within the hollow annular walls of the heat pipe [18] effects high degrees of spatial temperature uniformity and stability in the central region of the furnace cavity. The furnace accommodates a platinum growth crucible 7 cm in height by 8 cm in diameter with a capacity of roughly 230 cm$^3$ of growth solution.

A tubular steel frame structure provides support for both the furnace and a puller unit mounted above. The furnace rests directly on a heavy-duty adjustable X–Y table mounted to the bottom cross-members of the frame. The puller unit is supported by the top cross-members of the frame. The puller features controllable rotation rate and rotation reversal periodicity and can be equipped with a variety of platinum seed rods and stir paddles to facilitate a range of stirring and seeding functions.

Power to the furnace’s resistance heaters is provided by a zero-crossover SCR controlled by an analog temperature controller. The control thermocouple is positioned in a small Inconel well mounted roughly halfway along the outer wall of the heat pipe as shown. Additional reference thermocouples are positioned in the crucible support plate, as shown. Temperature programming and data acquisition are coordinated by a desktop computer. Crystal growth runs were performed in the temperature range of 970 to 900°C using cooling rates ranging from 0.5 to 10°C/day.

Thermal characterization of the furnace was performed involving direct profiling of an unstirred growth solution with a calibrated, platinum-sheathed thermocouple assembly combined with heat transfer analyses to establish the validity and accuracy of the thermocouple measurements [16]. Such characterization indicated spatial temperature uniformity within $\pm 1.9\degree C$ throughout the entire growth solution volume. Temperature stability over several days at any single location in the solution was better than $\pm 0.3\degree C$. Run to run repeatability of the time-averaged temperature at a given location in the solution for a given furnace set-point was within $\pm 0.1\degree C$.

As intended, a principal performance feature of
the furnace system is freedom from the problem of copious spurious nucleation, identified as a critical issue in earlier work on high-temperature solution growth of KTiOPO$_4$ [5,9]. Following proper solution pre-treatment to dissolve any spurious crystallites that form during solution preparation and transfer, the growth of a crystal can typically proceed unimpeded to an extent limited only by the dimensions of the crucible.

4. Seeding process

An extensive set of experiments was devoted to investigation of the effect of seed orientation and
attachment, fluid convection, and bulk supersaturation on initial seeded growth in the furnace system. Details of these experiments have been presented elsewhere [16]. Two major conclusions were reached.

First, the preferred seed attachment technique involved ultrasonically drilling and threading a small KTiOPO₄ crystal and securing it onto the end of a threaded platinum seed rod. There was no evidence of any problem associated with the consequent advancement of a growing crystal over and around the rod.

Second, within the investigated ranges of operating parameters, the achievement of initially uniform and flaw-free growth off a seed crystal was determined to require the controlled dissolution of the original seed surfaces prior to initiation of supersaturation and consequent growth. It is assumed that this necessity has as its basis a surface degradation phenomenon that occurs during the brief interval the seed crystal is exposed to the air inside the heated furnace cavity prior to its immersion in solution. The controlled surface dissolution in turn requires temperature controllability and repeatability in the solution to within ±0.5°C and a seed mounting secure enough to ensure integrity in the face of dissolution.

Both naturally-faceted crystals produced through induced nucleation and fabricated parallelepipeds cut from larger boules were used as seeds. In all cases, the transition from initial surface dissolution to faceted, stable growth was marked by a thin "veil" of solution inclusion, in a manner identical to that observed under similar conditions in many crystal growth operations from aqueous solution. Fig. 3 shows such a seeding veil.

5. Avoiding solution inclusion

As additional set of experiments was devoted to treatment of a chronic flawing problem whereby volumes of growth solution would become trapped and included in growing crystals. Room-temperature flow visualization analyses and crystal growth experiments in the heat pipe based furnace system were correlated through application of recently-developed qualitative theory of interfacial instability in crystal growth from solution [19–21]. The aim of the work was to establish a method for orientation and imposed motion of a crystal growing in the solution enabling reproducible avoidance of solution inclusion through the duration of the growth process.

The room-temperature flow simulation involved borosilicate glass crucibles, crystal models milled from acrylic plastic, and water as the model fluid. Flow visualization was enabled both by dye injection and by sheet beam illumination of suspended aluminum particles using a argon laser. Model scaling for dynamic similarity was greatly simplified by the fact that, due to the high degree of spatial temperature uniformity throughout the growth solution in the heat pipe furnace, the possibility of natural buoyancy-driven convection could be ignored. Thus, the only dimensionless groups to be accounted for in simulating the flow patterns around growing crystals were the Ekman number and a dimensionless characteristic time. The latter was involved in scaling the flow transients associated with start-up, stoppage, and reversal of crystal rotation.

Flow simulation and inclusion flawing experiments were performed for a variety of crystal orientation configurations, seed shaft rotation rates, and rotation reversal periodicities. Details of
these experiments are presented elsewhere [16,22]. A number of conclusions were reached.

First, solution inclusion phenomena were clearly correlated with fluid flow patterns. Second, in particular, bands of solution inclusion appeared to form on regions of growing surfaces immediately beneath stable regions of stagnant, uncirculating growth solution. Third, by varying the crystal orientation configuration and rotation pattern, patterns of stable solution stagnation could be altered or eliminated. Finally and most important from a technological standpoint, the preferred configuration we have found for avoiding solution inclusion flaws involves having a growing crystal mounted on the end of a platinum seed rod with a 90° bend roughly 12 mm from its end. The crystal is submerged roughly midway between the solution surface and the crucible bottom and rotates with periodic reversal, thereby traversing through the solution at some radius from the crucible centerline.

Fig. 4 shows crystals grown in the heat pipe furnace system using the surface dissolution seeding process and the 90° crystal orientation configuration. The overall process takes about 10 days. Numerous such crystals have been produced using two identical furnace systems.

6. Characterization of material grown

A series of characterization experiments was performed on KTiOPO₄ crystals grown in the heat pipe furnace system. Impurity analyses were performed using both spark source mass spectroscopy and inductively coupled plasma spectroscopy. In general, metallic impurity levels were below 5 ppm. IR and UV/visible transmission spectroscopy was performed on polished crystalline specimens. In all cases, the UV cutoff was at roughly 350 nm, typical of KTiOPO₄ grown by other techniques [9,14]. Slight OH⁻ incorporation was noted in some samples. Although quantitative comparative measurement was not made, typical of KTiOPO₄ grown from high-temperature solution, the extent of OH-incorporation was much less than that commonly found in KTiOPO₄ grown via hydrothermal processes [14].

A Q-switched Nd : YAG laser was employed in a series of measurements of the second harmonic generation properties of the grown material. The beam featured an energy of 46 mJ, a pulse width of 8 ns, and a diameter of 2.7 mm. KTiOPO₄ samples were oriented and fabricated with optical faces perpendicular to the optimal direction for second harmonic generation. For a typical set of

Fig. 4. KTiOPO₄ inclusion-free crystals and fabricated plate.
experiments performed on a prepared KTiOPO₄ specimen 8 × 8 mm² in cross-section and 3.5 mm in path length, the doubling efficiency was measured to be 25%, the wavefront distortion less than one-quarter wave at 633 nm, and the temperature bandwidth 22°C cm. These values are roughly equivalent to the best reported for KTiOPO₄ grown by other techniques. In a number of specimens 10 × 10 mm² in cross-section, irregular-shaped regions were observed leaving birefringence slightly different from the rest of the specimen. The optimal angle for second harmonic generation was thus slightly altered in these regions. The origin of these inhomogeneities is currently under investigation. No evidence of ferroelectric domain structure was observed in any of the grown material [23].

7. Summary

A process has been developed for crystal growth of KTiOPO₄ from its solution in K₆P₄O₁₃ using a seeded, slow cooling technique. A new furnace system was designed and constructed for use in the process, its key feature being a sodium-filled Inconel heat pipe providing for a high degree of spatial temperature uniformity throughout the growth solution. Initial surface dissolution appears necessary to achieve flaw-free growth immediately off a seed. Avoidance of solution inclusion flawing in advanced stages of growth requires a crystal orientation configuration and rotation pattern that does not give rise to stable regions of uncirculating growth solution. Through the process, 10-day growth runs routinely produce flaw-free crystals large enough to yield plates 10 × 10 × 7 mm³ oriented in the optimal direction for second harmonic generation having properties measured to be at least as good as KTiOPO₄ grown by other methods.

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References