Growth of KTiOPO$_4$ crystals by flux technique and their characterization

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Single crystals of KTiOPO$_4$ (KTP) have been grown by flux technique using K$_6$P$_4$O$_{13}$ flux. Crystals up to 3×2×1 mm$^3$ in size were grown by slow cooling and spontaneous nucleation when high temperature solution was cooled down to room temperature with the rate of 7°C/h. The structure and quality of the grown crystals were characterized by X-ray diffraction (XRD), Fourier transform infrared (FTIR) and Optical Transmission analysis. The surface morphology of the grown crystals was studied by scanning electron microscopy (SEM).

Keywords: Crystal growth, Non-linear optical materials, Flux growth, KTiOPO$_4$, Characterization

1 Introduction

Potassium titanyle phosphate (KTP) is an excellent non-linear optical crystal and the best frequency doubling material for 1064 nm Nd$^{3+}$ emission of Nd:YAG lasers, which is widely used in non-linear optical devices$^1$. Due to its large non-linear optical coefficient (10 times KDP), high damage threshold, high thermal stability and low walk off angle, KTP finds many applications in frequency doubling and mixing. It also finds wide applications in E-O modulators and Q-switches because of its high electro-optic coefficients and low dielectric constants$^2$. As KTP undergoes partial decomposition on melting at 1323 K, the melt growth technique cannot be employed for its crystal growth. Therefore, in order to obtain useful large single crystals, two main growth methods, namely, the hydrothermal method and the flux method are used. Since the hydrothermal growth technique requires rather special high pressure steel vessels with noble metal liners, so the flux-growth technique is currently the most popular method for obtaining large KTP single crystals. The significant advantages of using the flux process are: (i) It operates at atmospheric pressure and hence, does not require sophisticated pressure equipment so the crystals can be grown at atmospheric pressure, (ii) it is easy to design scaled-up furnaces and (iii) crystals can be grown without incorporation of water molecules which gives rise to considerable absorption in infrared region$^3$.

Different types of fluxes have been used for the growth of KTP crystals by flux method. But within these fluxes, polyphosphate (K$_6$P$_4$O$_{13}$) has identified as a viable high temperature solvent because of absence of foreign-ion and better morphology of the grown crystals$^4$. Owing to the high viscosity of the K$_6$P$_4$O$_{13}$ flux, the overall kinetic resistance for growing is large. Hence, a significant level of bulk supersaturation is required in the neighbourhood of the growing crystal. This bulk supersaturation is achieved by slow cooling of the solution$^5$. The amount of cooling rate during growth of KTP crystals by flux method depends on the type of the flux and technique adopted for the growth process. When top seeded solution growth (TSSG) technique is used, cooling rates as low as 0.5-2°C/day are sufficient to proceed, the growth process in the presence of seed crystal$^2$. When seed crystal is not introduced to the solution, nucleation occurs either on a cold finger or spontaneously inside the solution$^6$. This paper reports the growth of KTP crystals by spontaneous nucleation in solution using K$_6$P$_4$O$_{13}$ flux. The solution containing synthesized material was cooled down with different cooling rates to find out the effect of cooling rate on the growth of KTP crystals and the rate at which nucleation takes place spontaneously in solution. The grown crystals were subjected to different analysis and a comparison has been made between the properties of these crystals and the KTP crystals grown by other methods.

2 Experimental Details

2.1 Charge preparation

Starting materials including high purity KH$_2$PO$_4$, TiO$_2$ and K$_2$HPO$_4$ (Merck Company), with molar
ratio of 3:1:2 and total weight of 59.31 g were loaded in 75 ml Pt crucible and placed inside a pre-heated single zone furnace and got melted. MoO$_3$ with molar ratio of 0.002 mole per cent was added to the mixture as a modifier to reduce the viscosity of the flux. The crucible was kept at 1000°C for 16 h for more homogenization. Using pre-heated furnace avoided formation of bubbles, more frothing and dissociation of materials. The volume of the starting material reduced to almost half due to synthesizing process. The following reactions occurred in solution mixtures:

\[ 2\text{KH}_2\text{PO}_4 + 2\text{K}_2\text{HPO}_4 \rightarrow K_6\text{P}_4\text{O}_{13} + 3\text{H}_2\text{O} \quad \text{(1)} \]

\[ \text{KH}_2\text{PO}_4 + \text{TiO}_2 \rightarrow \text{KTiOPO}_4 + \text{H}_2\text{O} \quad \text{(2)} \]

### 2.2 Crystal growth

To study the effect of cooling rate on the growth process, the synthesized material kept at 1000°C was cooled to room temperature with different cooling rates. The experiments were carried out in a single zone box-type furnace with SiC heating elements. The furnace design ensured almost uniformity with only 2-3°C vertical and horizontal temperature difference along the charge material inside the crucible. In the first run, the crucible containing synthesized material was taken out of furnace and cooled down very fast in atmosphere. The resultant material was transparent, and appeared in single phase and glassy form and slightly yellowish because of 5% gold used in making Pt crucible (Fig. 1). The XRD analysis confirmed the amorphous nature of the synthesized material. These glasses were readily soluble in H$_2$O at room temperature. Upon dissolution in H$_2$O, there was no precipitation of either KTP or TiO$_2$. The remained water soluble titanium species was most probably a polytitanate.

When the crucible containing synthesized material was cooled down to room temperature inside the furnace with natural cooling of furnace (about 200°C/h), The resultant material appeared in two distinguishable phases: upper and lower ones. The upper one was transparent, glassy form and mild yellowish in colour dissolved in water at room temperature (Fig. 2a), whereas the lower phase was opaque, milky in colour and insoluble in water (Fig. 2b). Only by using HF and other acids such as H$_2$SO$_4$ and HCl, some percentage of this lower phase material was dissolved. Since KTP is not soluble in water but the flux (K$_6$P$_4$O$_{13}$) dissolves easily in water, the upper phase was found most probably to be the flux and the lower phase to be the KTP material. This was also confirmed by XRD and atomic absorption analysis. By reducing the cooling rate, it was observed that only for cooling rates lower than 25°C/h nucleation started inside the solution and about 10 KTP crystals with average size of 2x2x1 mm$^3$ were obtained. The grown crystals are almost transparent. This result is in good agreement with the report on spontaneous crystallization of Nb:KTiOPO$_4$ crystals on Pt rod grown with 20°C/h cooling rate.

The optimum cooling rate was found to be 7°C/h at which a large number of inclusion-free transparent crystals with average size of 3x2x1 mm$^3$ were grown. The crystals were mild-violet in colour because of MoO$_3$ modifier used in starting material. It was observed that the crystals were mostly formed either near to surface of melt or crucible wall because of higher supersaturation at these points. This spurious nucleation was the result of low level of spatial temperature uniformity in supersaturated solution.
because single zone furnace was used for growth process. The crystals were separated from the melt using hot water. Figure 3 shows some of the grown crystals. Only 70 per cent of the weight of KTP material in solution was converted to single crystals.

3 Characterization

3.1 X-ray diffraction studies

Powder X-ray diffraction studies were performed on the grown crystals to identify the phase formation and degree of crystal perfection. X-ray powder patterns of KTP were recorded using Bruker D4 X-ray diffractometer. Monochromatic intense X-ray of wavelength 1.5418 Å (CuKα) was used. The powder X-ray diffraction spectrum is shown in Fig. 4 which agrees well with data of ASTM standard for KTiOPO₄. The powder diffraction data were used to calculate the lattice parameters by the least square fit method and values were obtained \( a = 12.83 \) Å, \( b = 6.38 \) Å and \( c = 10.36 \) Å. These values are also in good agreement with the values reported in the literature.

3.2 Transmittance

The transmittance of the grown crystals was measured using a Shimadzu model UV-visible-1650 spectrophotometer in the spectral region 200-800 nm. Measurement was carried out on a single crystalline piece which was polished to 1 mm thickness using alumina abrasive powder. Fig. 5 shows the transparency curve of the KTP crystal grown by spontaneous nucleation. The curve has cut-off wavelength at 342 nm but there is no sharp fall in transmission at this UV cut off.

This shape of absorption edge and the presence of two other absorption peaks at 440 nm and 625 nm can be due to incorporation of different type of impurities into the grown crystals. Some of these impurities are flaws. The entrapment of liquid in a growing crystal is probably the most common macroscopic flawing effect caused due to the non-uniform supersaturating across the surface of the growing crystal which was occurred in our growth process. It was observed that the optical transmission spectrum of the grown crystals is consistent with the properties of KTP. But decrease in optical quality compared to the optical quality of the KTP crystals which are grown by TSSG technique, is due to using higher cooling and growth...
rates in our case. Our KTP crystals have been grown with cooling rate almost 100 times greater and growth rate three times higher than those values at which good quality KTP crystals have been grown by TSSG technique.

3.3 FTIR measurement
The vibrational modes of the KTP in the sample were defined with the help of a SHIMADZU 8400S FTIR infrared spectrometer in the region 400-4000 cm$^{-1}$. No mode was observed above 1200 cm$^{-1}$ and the spectrum between 400-1200 cm$^{-1}$ has been shown in Fig. 6. For making IR pellets, spectroscopic grade of KBr was used. KBr was dried at 120°C for about 12 hr.

KTP has an orthorhombic structure and belongs to the acentric point group mm 2 (space group Pna2$_1$), and each cell contains 8 formula units$^{11}$. Its structure consists of tetrahedral PO$_4$ ion and octahedral TiO$_6$ with potassium in larger void$^{12}$.

Herzberg$^{13}$ calculated four normal modes of tetrahedral PO$_4$ ion at $v_1=980$ cm$^{-1}$, $v_2=363$ cm$^{-1}$, $v_3=1082$ cm$^{-1}$ and $v_4=515$ cm$^{-1}$. $v_1$, $v_2$ are Raman and $v_3$, $v_4$ are Raman and IR active modes$^{13}$. Seyyidoğlu$^{12}$ observed these modes of vibrations at $v_1=938$ cm$^{-1}$, $v_2=420$ cm$^{-1}$, $v_3=1017$ cm$^{-1}$ and $v_4=567$ cm$^{-1}$, and Uzeturk-Amour$^{14}$ also mentioned that the antisymmetric stretching modes were found between 1290 cm$^{-1}$ and 1050 cm$^{-1}$, and the symmetric modes between 1050 cm$^{-1}$ and 900 cm$^{-1}$. Hudson$^{15}$ and Nakamoto$^{16}$ stated that the highest frequency observed was due to antisymmetric stretching involving the terminal bond, the shortest bond $v_{as}$ P-O was observed around 1135 cm$^{-1}$ and we observed $v_3$ mode at around 1124 cm$^{-1}$. Kugel $et$ $al$.$^{11}$ described the $v_4$ mode localized between 450 cm$^{-1}$ and 575 cm$^{-1}$ with a major peak at 517 cm$^{-1}$ and we observed at $v_4=557$ cm$^{-1}$.

The vibrational modes of a perfect isolated MO$_6$ octahedra can be decomposed into two pure bond stretching vibrations $v_1$, $v_2$, two inter bond angle bending vibrations $v_3$, $v_6$ and finally, two remaining vibrations $v_4$, $v_5$ considered as combinations of stretching and bending. $v_3$, $v_4$ and $v_6$ are IR active and $v_1$, $v_4$ and $v_5$ are Raman active modes. Kugel $et$ $al$.$^{11}$ reported $v_1=700$ cm$^{-1}$, $v_2=637$ cm$^{-1}$ and $v_5=269$ cm$^{-1}$. Because of FTIR instrumentation, in our results, the peaks over 400 cm$^{-1}$ were observed at $v_1=707$ cm$^{-1}$ and $v_2=640$ cm$^{-1}$. All these results confirmed the growth of KTP on the basis of flux method.

3.4 Surface analysis
Analysis was carried out on the surface of the as-grown and etched crystals using SEM. Fig. 7 shows SEM picture of the grown crystals. A comparison between the morphology of these crystals and ideal morphology of KTP crystals shows that only some of the facets out of 14 facets have been formed. Fig. 8 shows a part of circular steps with different spacing grown on the surface of the as-grown crystals. These circular steps are normally formed by the latest solution droplets at the final stage of the growth process. Similar circular steps have also been observed on the surface of the KTP crystals grown by TSSG technique under 20°C/h cooling rate$^{10}$.

To study the surface of etched crystals, crystalline samples were kept in a 37% HCl solution for 60 min. Fig. 9 shows the surface of the etched crystals. The surface is covered by wave-like steps on which etch pits are produced. This wave-like surface is the result

![Infrared spectrum of the grown KTP crystals](image)

Fig. 6—Infrared spectrum of the grown KTP crystals

![SEM picture of the grown KTP crystals](image)

Fig. 7—SEM picture of the grown KTP crystals
Crystal growth via spontaneous nucleation in 100 cm³ crucible always yields this type of conglomerate, hopper-type growth\(^8\). This is a result of supersaturation gradients in the solution due to its viscosity, which is estimated to vary between 60-500 cp when temperature of the solution varies from 1000 to 800°C. Using single zone box type furnace in our case, favoured the horizontal and vertical temperature gradients along the crucible. The reduction in size of crucible overcomes multiple nucleations but the volume of charge material and resultant grown crystals will be reduced.

Fig. 10 shows the dendrite pattern on the surface of the etched crystals. This again shows that crystals have grown under non-equilibrium condition. Both the etch pits with and without hollow cores observed on surfaces of the grown crystals. Figs 11 and 12 show the hollow core and non-hollow core etch pits,

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Fig. 8—Circular steps on the surface of the as-grown KTP crystals

Fig. 9—Wave-like steps on the surface of the etched KTP crystals

Fig. 10—Dendrite pattern on the surface of the etched KTP crystals

Fig. 11—Hollow core etch pits on the surface of the etched KTP crystals

Fig. 12—Non-hollow core etch pits on the surface of the etched KTP crystals
respectively on the surface of the grown crystals. Similar patterns have been observed on the surfaces of the KTP crystals grown by TSSG technique\(^1\). These hollow cores (spike) etch pits are formed because of a dissolution catastrophe occurring around a dislocation with a screw component.

4 Conclusion

The effect of cooling rate on the growth of KTP crystals by flux method was studied. It was observed that when synthesized material (at 1000°C) was cooled down to room temperature with high cooling rate only amorphous materials in either single phase or two separated phases were obtained. The crystallization of KTP crystals by spontaneous nucleation was started only for cooling rates lower than 25°C/h. KTP single crystals with limited sizes (3×2×1 mm\(^3\)) were grown for 7°C/h cooling rate. XRD, FTIR and optical transmission analysis revealed the formation of KTP structure for the grown crystals. Optical transmission studies showed the incorporation of more defects into the KTP crystals grown by spontaneous nucleation which was also confirmed by micro morphological studies.

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References