

Habit control of deuterated potassium dihydrogen phosphate crystal for laser applications

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Abstract. In this study we investigate the habit of partially deuterated potassium dihydrogen phosphate (DKDP) crystals in the presence of Al^{3+} ions. We have grown single DKDP crystals in (50wt% and 80wt%) partially deuterated solutions and in solutions doped with Al^{3+} ions (2 ppm) by the point-seed rapid growth technique at controlled supercooling ($\Delta T=10^\circ\text{C}$). The growth length of each crystal face was measured and the aspect ratio was calculated. We found that crystals grown in partially deuterated solutions are similar in aspect ratio, while, crystals grown in deuterated solutions doped with Al^{3+} ions showed a relative change in aspect ratio, the crystal increased in size in the pyramidal direction (vertical axis direction). Crystal characteristics were also analyzed by X-ray diffraction, FTIR and Raman spectroscopy. We have speculated that the relative habit modification is due to a probably adsorption and inclusions of Al^{3+} ions in the prismatic section of the crystal.

1. Introduction

In recent years, high-power laser facilities require optical devices as a part of its design. KDP and DKDP crystals are recognized for its special optical properties. Those crystals can be grown sufficiently large to fulfill the requirements of the design. However for the optimization in the production of those crystals, it is crucial to control the habit which is given by the aspect ratio (ratio of crystal dimensions along its crystallographic axes, X, Y, Z and the constant angles between the faces).

In previous studies, we have reported the habit and growth kinetics of KDP crystals in presence of metallic (Cr^{3+} , Fe^{3+} , Al^{3+} and Pb^{2+}) ions, these impurities showed the ability to control the shape and growth faces [1, 2]. Large information on KDP crystal can be found. However, limited information is available on the habit of partially deuterated DKDP crystals. A recent study on the habit of DKDP crystal in the presence of Al^{3+} ions (1ppm) was reported, where Al^{3+} ions cannot be used as habit modifier in the presence of EDTA solutions [3]. Another interesting study found was the habit control of KDP and DKDP crystals without impurities using the rapid growth method [4]. In these reports, high deuterium concentration levels (98%) were used. Recently, high-power laser requires 70~80% deuterated DKDP crystals. Therefore, data in partial deuterated concentrations are required.

In this work, the influence of Al^{3+} ions on the habit (referred as, aspect ratio) of DKDP crystals is studied in two levels of deuterated solutions. The seed point technique and controlled supercooling conditions are applied to evaluate the possibility to control the habit and to obtain large bulk crystals.



2. Experimental Procedure

Two partially deuterated solutions (D₂O-H₂O, 50wt% and 80wt% in D₂O) were prepared using deuterium water (Heavy water) 99.8% in D₂O (Isotec Inc.) and distilled water deionized. The Solutions were saturated with extra pure reagent grade KDP and Aluminum standard solution (Kanto Kagaku) was used as impurity to obtain a doped solution (Al³⁺ ions, 2ppm). The doped and un-doped solutions were previously filtered, over-heated to 60 °C for 4 h and cool-down to 40°C. Seed crystals were prepared by spontaneous nucleation of KDP solution and then selected seed crystals were grown in deuterated solutions. The obtained DKDP seed crystal was glued in a crystal holder as a point seed and set into a small scale jacketed crystallizer (30ml vol.). The supercooling condition ($\Delta T=10^{\circ}\text{C}$) was controlled with a programmable temperature controller at a rate of 0.5 °C /h. Before and after the growth, the crystal size was measured between the faces in the three crystallographic (X, Y and Z) axes and the aspect ratio was calculated. The characteristics of the grown crystals were also verified by X-ray diffraction, FTIR and Raman spectroscopy.

Previous to the experiments, the impurity and the impurity concentration were first evaluated between three different ions (Pb²⁺, Cr³⁺ and Al³⁺). Scanning Electron Microscope (SEM) was used to evaluate the habit change of the crystal in a wide range of impurity concentrations (up to 100 ppm).

3. Results

The results on the selection of impurity and impurity concentration are shown in figure 1. SEM pictures shows the habit of DKDP microcrystals nucleated from deuterated solution 50wt% doped with Pb²⁺, Cr³⁺ and Al³⁺ ions at 2 ppm concentration. The habit of microcrystals grown in the presence of Pb²⁺ and Cr³⁺ ions did not show any considerable change (see, figure 1 (a) and (b), respectively). However, the crystals grown with Al³⁺ ions showed a relative habit change. The crystal growth increase was clearly observed in the pyramidal direction (z-axis direction). At impurity concentration higher than 2 ppm, the crystal became slender and finally showed a needle shape (20 ppm). In the case of Pb²⁺ and Cr³⁺ ions, the crystals were tapered and needle shape (data not show here). From these observations, Al³⁺ ions and 2 ppm were selected as impurity and impurity concentration.

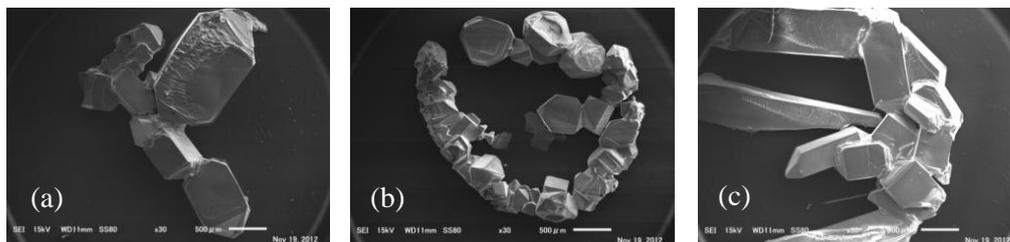


Figure 1. Habit of DKDP microcrystals grown from doped solutions (a)Pb²⁺, (b)Cr³⁺ and (c)Al³⁺ ions. (50wt% deuterated solutions with 2 ppm impurity concentration)

After the impurity selection, single DKDP crystals were grown in a crystallizer in two different solutions. One is, in deuterated solutions 50wt% and 80wt% and the other is in deuterated solution doped with Al³⁺ ions. The habit of each crystal grown in these solutions can be seen in figure 2. Habit of crystals grown in 50wt% and 80wt% deuterated solutions free of Al³⁺ ions are shown in figure 2(a) and figure 2(c), respectively. Deuterium concentration increase in the solution did not affect the crystal habit. However, in solutions doped with Al³⁺ ions a relative habit change can be observed (see, figures 2(b) and 2(d)) where the crystals showed an increased growth in the pyramidal direction (z-axis) similar to those crystals showed in figure 1(c).

Size of grown crystals was measured and the aspect ratio was calculated. Average values of the aspect ratio are shown in table 1. The calculations showed that the x/y ratio of the crystals grown from deuterated solutions were similar compared to the x/y ratio of their seed crystals. In contrary, z/x and z/y ratios of crystals grown in doped Al³⁺ ions exhibited an increased value indicating a habit change. In some cases, slightly tapering effect was observed on the prismatic face (100) (see, figure 2(b)).

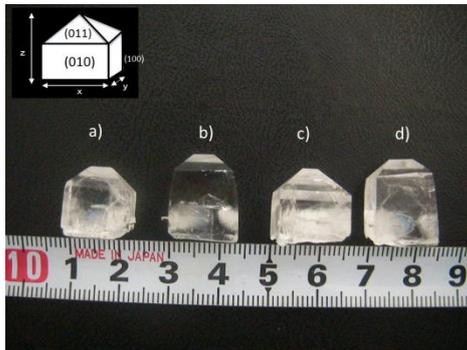


Figure 2. Habit of DKDP crystals grown in partial deuterated solutions and in solutions doped with Al^{3+} ions.

- (a) DKDP crystal in 50wt% D_2O ,
- (b) DKDP crystal in 50wt% D_2O with Al^{3+} 2ppm
- (c) DKDP crystal in 80wt% D_2O
- (d) DKDP crystal in 80wt% D_2O with Al^{3+} 2 ppm

Table 1. Aspect ratio change of DKDP crystals in presence of Al^{3+}

Impurity content (ppm)	D_2O in solution wt%	Seed crystals			Grown crystals		
		x/y	z/x	z/y	x/y	z/x	z/y
0	50	1.48	0.89	1.31	1.48	1.09	1.61
	80	1.40	0.91	1.27	1.38	1.00	1.38
2 ppm	50	1.45	0.87	1.25	1.47	1.37	2.01
	80	1.45	0.91	1.31	1.40	1.35	1.88

On the other hand, grown crystals were also analyzed to see the effect of the impurity concentration in the internal structure. The X-ray diffraction patterns of DKDP powder was used to check the DKDP crystal structure. A Rigaku X-Ray Diffractometer (RINT 2000) was used for the analysis. The X-ray pattern of DKDP crystals grown in 50wt% deuterated solution and with doped Al^{3+} ion at 2 ppm, are compared and shown in figure 3. The diffraction patterns were similar in both cases. From these results can be assumed that Al^{3+} ions do not affect the internal structure.

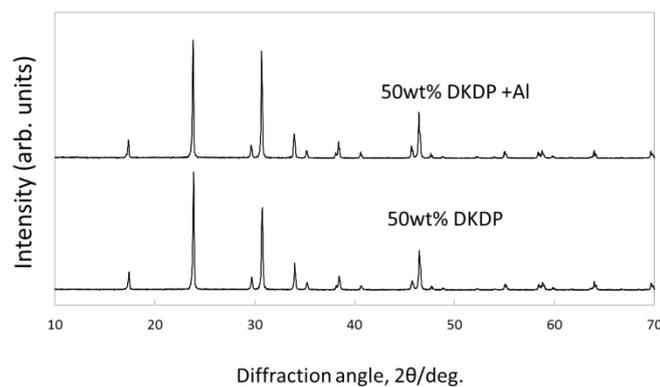


Figure 3. X-ray powder diffraction patterns of DKDP (50wt%) and DKDP (50wt%) doped with Al^{3+} (2 ppm)

The presence of deuterium content in the crystal was examined with a Jasco Raman Spectrometer NRS-5000. Samples of DKDP crystals grown in partially deuterated solution (50wt% and 80wt%) were analyzed and for comparison a KDP crystal was also used. The Raman spectra of the samples are shown in figure 4. Here, the absorption spectra shift (930 cm^{-1}) increased according the deuterium concentration. The spectral shifts in this range indicate us the presence of deuterium in the crystal and the replacement of hydrogen by the deuterium.

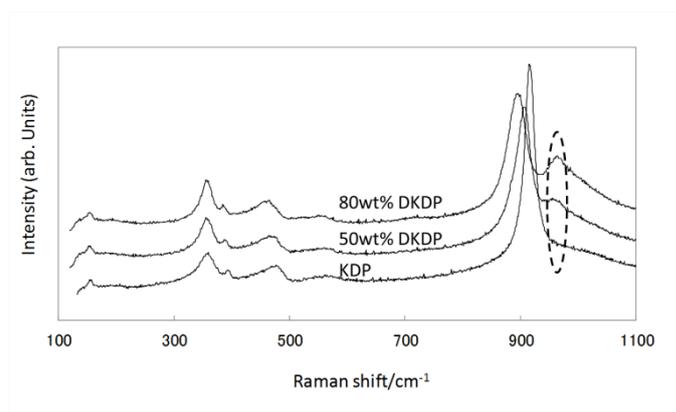


Figure 4. Raman spectra of pure KDP, 50wt% DKDP and 80wt% DKDP

On the other hand, the DKDP crystals grown in deuterated solution 50wt% and with Al^{3+} were analyzed using an Infrared Spectrometer FT/IR-6100 (Jasco). The internal vibration modes of hydrogen was observed in a spectral range area between $4000\sim 400(\text{cm}^{-1})$. Result of the analysis is shown in figure 5. Absorption bands were detected at relatively high-frequency region. O-H stretching appeared in a 3500 cm^{-1} followed by the P-O-H asymmetric stretching at $2900\text{ (cm}^{-1})$. And finally, O=P-OH stretching appeared at 2400 and $1600\text{ (cm}^{-1})$ respectively. The O-H stretching adsorption band was relatively different. It is probably caused by an inclusion of Al^{3+} into the crystal. The other modes remain similar.

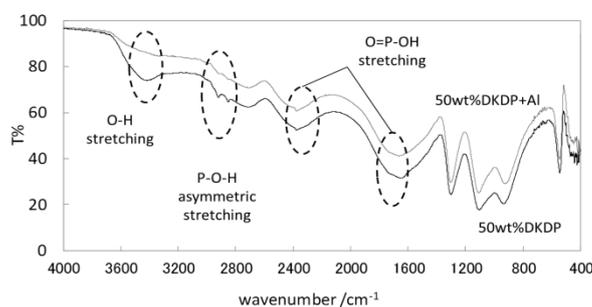


Figure 5. IR spectra of DKDP crystals grown in 50wt% deuterated solution and deuterated solution doped with Al^{3+} ions (2 ppm).

From the results described above, we can estimate that Al^{3+} ion would be a candidate to be used as a DKDP crystal habit modifier. However, to determine the factors that control the crystal habit more effectively is still necessary to understand the growth kinetics at different growth conditions (of deuterium concentration, supersaturation and temperature, etc.). As a continuation of this work, a study is under investigation and it will be reported elsewhere.

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