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Growth of KDP Single Crystals in Aqueous Solution

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수용액중에서 KDP단결정의 육성

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ABSTRACT

The growth of KDP single crystals were carried out by the temperature decrease method and the constant temperature method. The temperature coefficients of solubility were positive over the range 20-80℃. The solubility of KDP obeyed the van't Hoff equation and the heat of dissolution was about 4 kcal/mol. Large KDP single crystals have been successfully grown at temperature of 31℃ in aqueous solution with seed crystal. The tapering of KDP single crystals are affected by three parameters : acidity, supersaturation and temperature. KDP-ADP crystal could be grown at temperature of 33℃ in aqueous solution.

요　　약

KDP단결정의 육성을 서냉법 및 정온법에 의해 행하였다. KDP용해도의 온도계수는 20-80℃의 측정온도 범위에서 positive였다. KDP의 용해도는 van't Hoff식에 잘 따랐으며 용해열은 약 4kcal/mol이었다. KDP종자결정은 수용액중의 육성온도가 30℃일때 큰 결정으로 성장하였다. KDP단결정의 tapering효과는 산도, 과포화 및 육성온도에 의존하였다. KDP-ADP결정은 수용액중 33℃의 육성온도에서 얻을 수 있었다.

1. INTRODUCTION

Recently, potassium dihydrogen phosphate (KDP) single crystal as the nonlinear optical material has become very important in the development of laser engineering. The single crystals of KDP have been attracted by its high efficiency of frequency conversion and high damage threshold against high power lasers[1, 2]. KDP single crystals grow from aqueous solution which are supersaturated. The growth methods are based on the magnitude of the solubility and its variation with temperature. In most reports, one of the issues in crystal growth is how to grow a large sized KDP single crystal of high perfection[3-15]. As far as is known to the authors, a study on the growth of KDP-ADP crystal has not been reported.

In the present paper, we report the results of the temperature dependences of percent solubility and the general features for the growth of large KDP single crystals of good quality. In addition, the tapering effect of KDP single crystals and the growth of KDP-ADP crystal will be also reported.

2. EXPERIMENTAL

A commercial KH_2PO_4(KDP) particles were used for the solubility measurement and crystal growth. Solubilities in aqueous solution were carried out at desired temperature and were determined by the weight loss method. Solubilities of KDP were measured at temperatures over the range 20-80℃. Growth runs of KDP single crystals were carried out by the temperature decrease method and the constant temperature method. The techniques used in this work are usually appropriate for the growth of aqueous soluble crystals such as KDP and ADP($NH_4H_2PO_4$). KDP particles as a nutrient were placed in the high temperature zone, while seed crystals were placed in the low temperature zone, because of its positive temperature coefficient of solubility. The growth time of seed crystals was usually longer than two weeks. In order to investigate the tapering effect, the tapering angles were previously measured from photographs of the KDP single crystal. Preliminary growth experiments of KDP-ADP crystal were attemped by the constant temperature method. The growth runs were carried out at temperatures below 40℃ in ADP solution with as-grown KDP single crystal. The identification of the grown single crystals was performed by the X-ray diffraction (XRD). Cracks of the grown single crystals were investigated by the optical microscopy. The growth rates and morphologies of the grown single crystals were observed by the microscope.

3. RESULTS AND DISCUSSION

Solubilities were measured as a function of temperature over the range 20-80℃. Figure 1 shows the solubility of KDP as a function of temperature in aqueous solution. In turns out that the temperature coefficient of solubility is positive. This fact indicated several features of

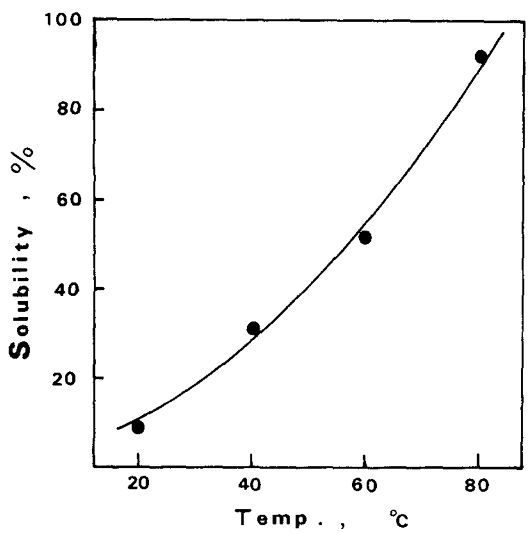

Fig. 1. Weight percent solubility of KDP as a function of temperature in aqueous solution.

importance to crystal growth, i.e. it is eventually required to proceed the crystal growth with supersaturation provided by a temperature difference where the KDP particles as a nutrient were placed in the high temperature zone, while seed crystals were placed in the low temperature zone. With this arrangement it was expected that the dissolved nutrient would be efficiently used to grow KDP single crystals on the seed without spontaneous nucleation occurring. In order to investigate the dissolution behavior of KDP in aqueous solution, the solubility was re-plotted as a relation of log (solubility) with 1/T as shown in Fig. 2. The figure reveals that the van't Hoff equation was well obeyed. From the slope of

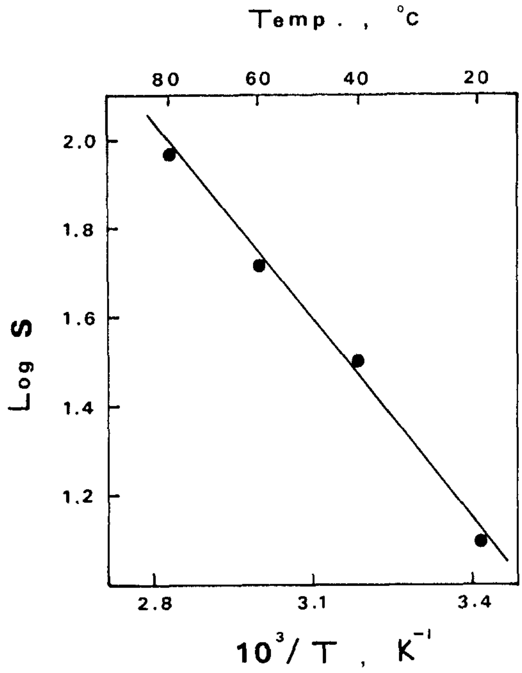

Fig. 2. Log solubility(Log S) of KDP as a function of 1/T in aqueous solution.

Fig. 2, the heat of dissolution, $\triangle H$, was calculated to be about 4kcal/mol. This value agree very well with those reported by H. Takubo et al.[11].

Growth techniques for KDP single crystals with high solubility and a large positive temperature coefficient are very appropriate the following methods ; the temperature decrease method and the constant temperature method. Based on the results of solubilities, synthesis of seed crystals was achieved by slow cooling of the saturated solution at 80℃, i.e. the temperature decrease method. As a result, spontaneously nucleated crystals were obtained at the lower part of the growth tank. The growth rate of KDP single crystal depend on supersaturation, cooling rate and other factors. Preliminary growth runs of seed crystals with euhedral morphology were carried out by the constant temperature method at temperatures over the range 25−45℃. As a result, the large single crystals of KDP were successfully grown under the following conditions : temperature of growth region, 31℃ ; vertical temperature difference, 3−4℃ ; pH of the solution, 4. Under such conditions, seed crystals of KDP are generally grown at a rate of approximately 1mm/day in the direction of the c−axis. A typical grown crystal is shown in Fig.3. This single crystal has morphologies bounded by (100), (010), (101) and (011) faces. As shown in Fig.4, also, the single crystals grown under these conditions were confirmed by XRD to be only the KDP. On the other hand, the grown single crystals tend to have inclusions and cracks when they grow rapidly along the a−axis. In order to grow the KDP single crystals of good quality, therefore, it is important to grow only on the c

－axis.

KDP single crystals have been examined for the tapering effect. Figure 5 shows this situation. The tapering of KDP single crystals are affected by three parameters : acidity, supersaturation and temperature. It has been observed that the tapering of KDP single crystals increases with acidity and decreases with supersaturation and temperature. Fig. 5 (b) shows that the tapering effect is more pronounced at low supersaturation as shown in the result.

KDP and ADP single crystals are of interest

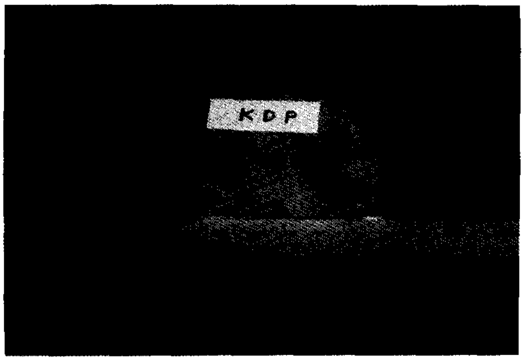

Fig. 3. Photograph of KDP single crystal grown by the constant temperature method.

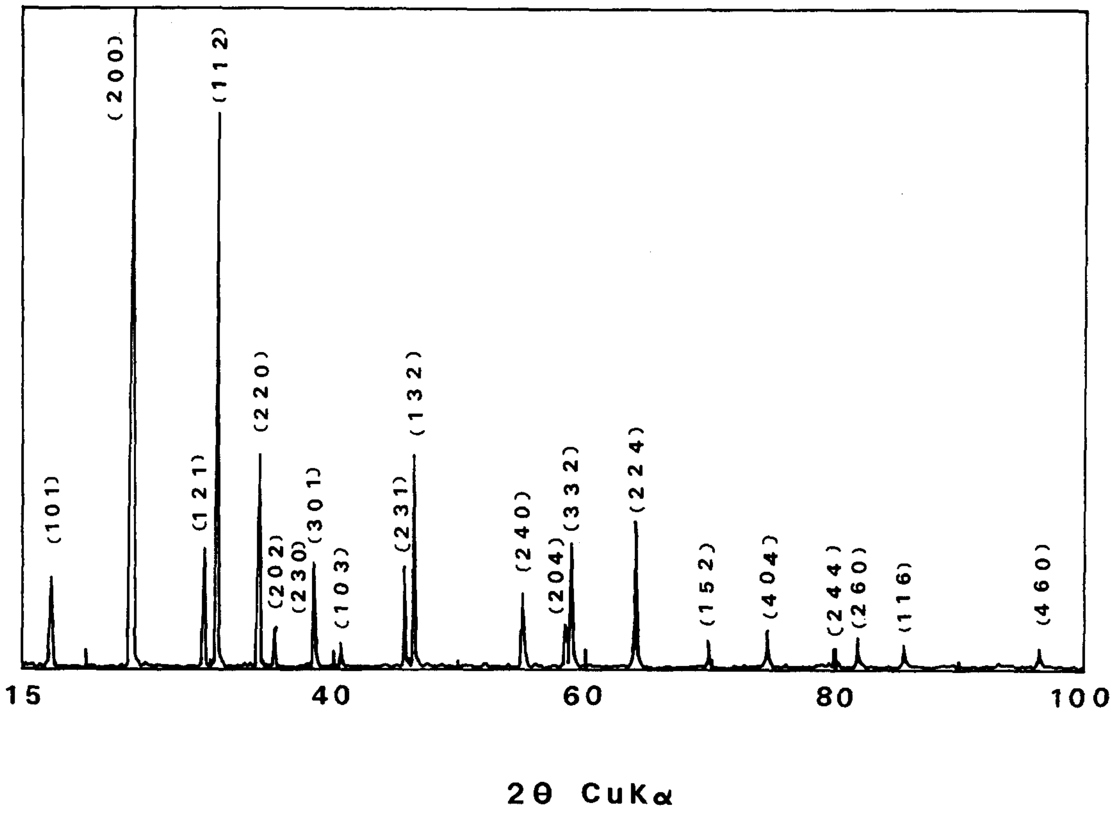

Fig. 4. X－ray diffraction profile of KDP single crystals.

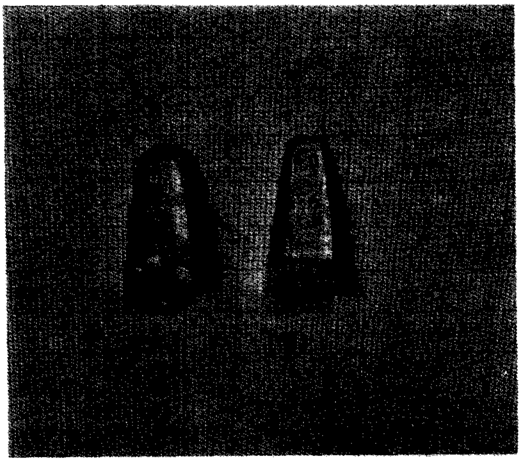

Fig. 5. Photograph of tapered KDP single crystals.

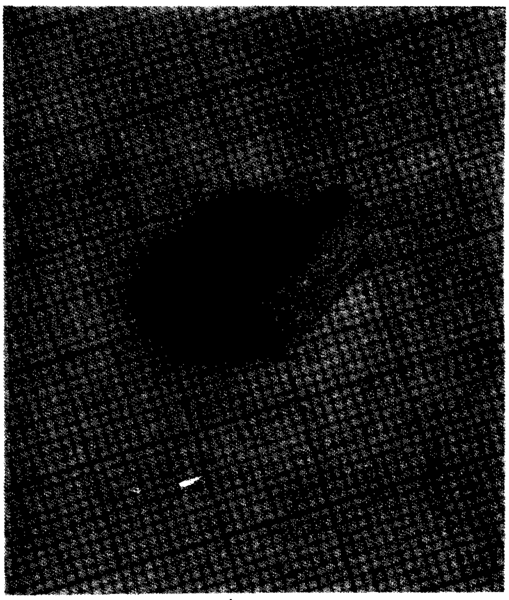

Fig. 6. Photograph of polished KDP−ADP crystal.

because of the similarity of their crystal structures. Also, these single crystals grow from aqueous solution and the temperatures of crystallization are nearly similar. It was experimentally found that the KDP−ADP crystal can be grown under the following conditions, i.e. temperature of growth region 33 ℃ ; vertical temperature difference 3−4℃, where solubilities of KDP and ADP were large enough to proceed the growth. Figure 6 shows the photograph of polished KDP−ADP crystal. It was confirmed to consist of the laminated crystal of KDP−ADP.

4. CONCLUSIONS

Solubilities of KDP were measured at temperatures over the range 20−80℃ and the temperature coefficient was found to be positive in aqueous solution. The solubility of KDP obeyed the van't Hoff equation. The heat of dissolution with the solution was about 4kcal/mol. Large KDP single crystals could be grown at temperature of 31℃ in aqueous solution. Morphologies of grown single crystals tended to be bounded by (100), (010), (101) and (011) faces. In order to grow the KDP single crystals of good quality, it was important to grow only on the c−axis. The tapering effect of KDP single crystals increases with acidity and decreases with supersaturation and temperature. KDP−ADP crystal of good quality was usually grown at temperature of 33 ℃ in aqueous solution.

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