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Review

A study on the growth and properties of KTP single crystals

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KTP($KTiOPO_4$)단결정 육성 및 물성 연구

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Abstract KTP seed crystals were grown by the hydrothermal method and the properties of grown crystals were investigated by means of infrared spectrophotometer. The hydrothermal conditions for high growth rates of seed crystals are as follows: temperature ranges, between 430 and 450℃; hydrothermal solvent, 4m KF solution; temperature difference, $30<\triangle T<65$℃; filling %, 65 %; growth method, vertical temperature gradient method. Under these conditions, morphologies of the grown KTP single crystals tended to be bounded by (100), (011) and (201) faces and hydroxyl groups were observed in the grown crystals.

요 약 KTP 종자결정의 육성을 수열법에 의해 행하였으며, 육성결정의 물성은 적외분광 광도계를 이용하여 조사하였다. 종자결정의 육성에 있어 큰 성장속도를 나타내는 수열조건은 다음과 같다. 즉, 온도범위, 430~450℃; 수열용매, 4몰 KF용액; 온도차, $30<\triangle T<65$℃; 충진율%, 65%; 육성방법, 수직온도 구배법. 이와 같은 조건하에서 얻어진 KTP 단결정의 형태는 (100), (011), (201)면이 잘 발달하는 경향이 있었으며 그리고 육성결정 중에는 hydroxyl group이 존재하였다.

1. Introduction

Potassium titanyl phosphate, $KTiOPO_4$ (KTP), is known to have an orthorhombic structure, and space group P_n2_1 at room temperature. It is well known that the single crystals of KTP show excellent nonlinear optical properties like high nonlinear optical coefficient, high laser damage threshold, temperature stability of phase matching angle, transparency over a broad wavelength range, and chemical and thermal stability [1-3].

Because of these properties, KTP single crystals have been extensively studied from a point of view of the applications for nonlinear optics.

KTP is known to have an incongruent melting point with a partial decomposition [4]. This fact suggests that the hydrothermal method and the top-seeded method with flux are appropriate for the growth of KTP single crystals. Most of the KTP single crystals, which is commercially used in SHG(Second Harmonic Generation) of Nd : YAG laser, have been obtained by the top-seeded method. However, the laser damage threshold for flux grown KTP single crystals are at least an order of magnitude lower than that of the hydrothermally grown KTP single crystals [5]. Such a drawback has restricted some applications for flux grown KTP single crystals. Therefore, recently, the hydrothermally grown KTP single crystals are required for the nonlinear optical applications. However, one of the issues in the hydrothermal growth of KTP single crystals [5-12] is how to grow large sized crystals. On the ground of this point, in this paper we report the result of the features for the growth of large KTP single crystals. In addition, the optical properties of the hydrothermally grown KTP single crystals will be also reported.

2. Experimental

The starting particles of KTP for the crystal growth were prepared by the solid state reaction using KH_2PO_4 and TiO_2 mixture and the subsequent hydrothermal treatment in KF solution. The procedures for solubility measurements have already been reported [12]. Growth experiments of KTP single crystals were carried out in gold or platinum lined autoclave of a general alloy steel with Tuttle-Roy seal, a dimension of 10 mm inner diameter and 27 ml in capacity. Growth runs were carried out by the vertical or horizontal temperature gradient methods with seed crystals. These growth methods are expected that the dissolved nutrient is efficiently used to grow single crystals on the seed without any occurrence of spontaneous nucleation. Morphologies of the grown crystals were observed by optical microscopy. The optical properties of grown single crystals were investigated by infrared spectrophotometer (IR). The characteristic IR spectra were measured between 2.5 and 10 μm.

3. Results and discussion

The starting particles of KTP were synthesized as a single phase by the solid state reaction with KH_2PO_4 and TiO_2 at 800℃ for 24 hrs and subsequently hydrothermally treated at 250℃ for 48 hrs in 4 m KF solution. These KTP particles were used as a nutrient for the seed crystal growth. KF and K_2HPO_4 solutions were chosen as the hydrothermal solvents for the crystal growth of KTP from the results of ref.12. In order to select the concentration of these solvents, the preliminary growth runs with seed crystals were carried out under the several hydrothermal conditions. The results showed that the growth of seed crystals in these solutions above 3 m were relatively practical. On the other hand, the solubility of KTP in KF solution was greater than that for comparable conditions in K_2HPO_4 solution. This result indicates the great advantage of KF solution for obtaining large crystals. Therefore, 4m KF solution was determined as the most promising solvent for the growth of KTP seed crystals in this work.

A photograph of apparatus used for the hydrothermal growth of KTP single crystals is shown in Fig. 1. Growth runs with KTP seed crystals were carried out using several conditions and methods. From these results, the seed crystals revealed different growth features according to the growth conditions and methods. The effective growth of the seed crystals was difficult at temperature below 400℃. And the growth time of the seed cryatals was usually longer than four weeks. The techniques, such as the vertical or horizontal temperature gradient method used in this work, are usually adequate for the growth of KTP single crystals [12]. Here, growth runs by the horizontal temperature gradient method have the advantage to obtain the spontaneously nucleated crystals as a seed. But the growth rates along the c axis of seed crystals obtained by vertical temperature gradient method are higher than those by horizontal temperature gradient method. Fig. 2 shows a schematic diagram of autoclave with Tuttle-Roy type used for the

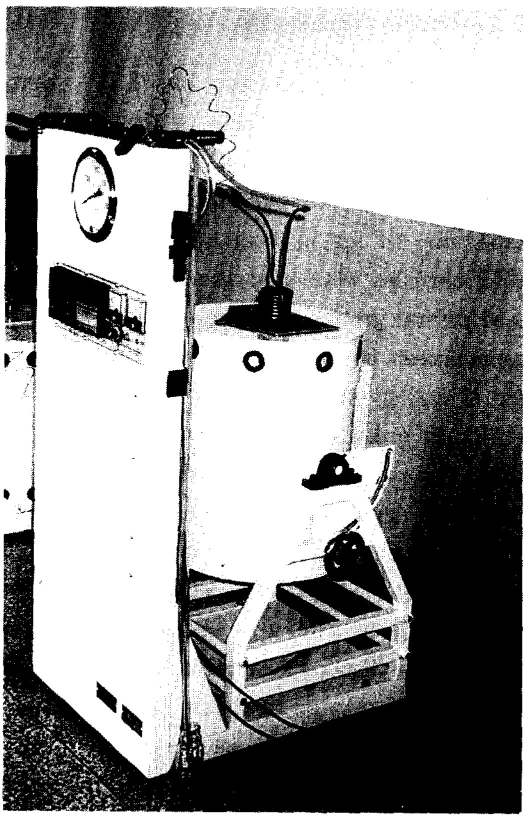

Fig. 1. Photograph of apparatus used for the hydrothermal growth of KTP single crystals.

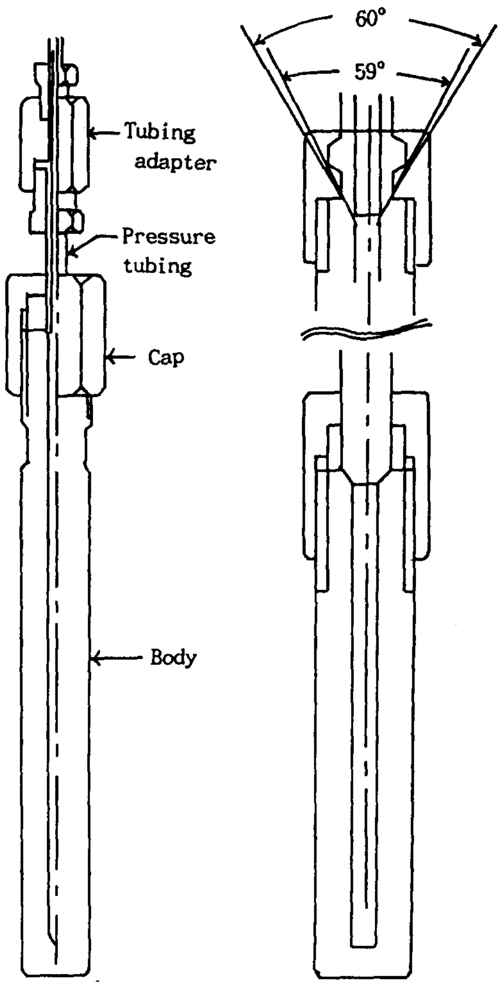

Fig. 2. Schematic diagram of autoclave used for the vertical temperature gradient method.

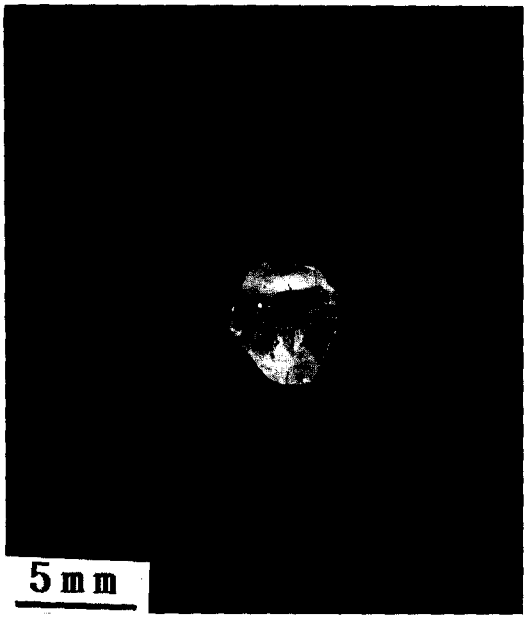

Fig. 3. Photograph of the typical KTP single crystal grown with seed crystal by the vertical temperature gradient method at 450℃ for 50 days in 4m KF solution.

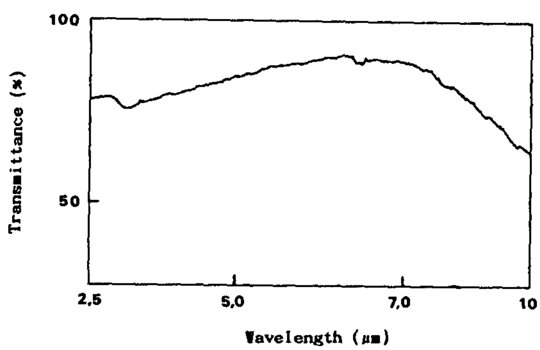

Fig. 4. IR spectra of the KTP single crystals grown at temperature between 430 and 450℃ in 4m KF solution.

vertical temperature gradient method.

From the above results, the growth runs have been examined for the hydrothermal conditions of temperature over the range of 430 ~ 450℃, hydrothermal solvent of 4m KF solution, temperature difference of $30 < \triangle T < 65$℃, filling of 65% and by the vertical temperature gradient method, where solubilities of KTP were large enough to proceed the growth. Under these conditions, the KTP seed crystals could be grown at a rate of approximately 0.1 mm/day in the direction of the c axis. A typical grown crystal is shown in Fig. 3. As a result, seed crystals with euhedral morphologies could be grown to about $5 \times 5 \times 4$ mm^3 in size.

The morphologies of seed crystals grown at temperature over the range from 430 to 450℃ in 4m KF solution are bounded by (100), (011) and (201) faces. These morphologies agree very well with those reported by Jia et al. [5]. On the other hand, the growth rates along the c and b axes were higher than that of the a axis. Such a growth behaviour is similar to that of flux grown KTP single crystals which are reported by Miyamoto et al. [13] and Sasaki [14]. It is known that the transparent range of KTP single cryatsls are between 0.35 and 4.5 μm[15]. The IR spectra of the hydrothermally grown KTP single crystals is shown in Fig. 4. The hydroxyl groups contained in the grown crystals show a broad band at around 2.7 μm due to the OH stretching and 6.2 μm due to the OH deformation [16]. It is considered that the drop of the transmittance around 8.0 μm is due to the P-O stretching. The magnitude of transmittance of the hydrothermally grown KTP single cryatals is considered to be influenced by the hydroxyl groups. According to ref. 5, however, it is considered that the performance of nonlinear optical applications, as well as flux grown KTP single crystals, may probably be very promising.

4. Conclusions

KTP particles used for the crystal growth were prepared by the solid state reaction of a stoichiometric mixture of KH_2PO_4 and TiO_2 and subsequently by the hydrothermal treatment. The hydrothermal conditions for high growth rates of KTP single crystals were as follows: temperature ranges, between 430 and 450℃ ; hydrothermal solvent, 4m KF solution ; temperature difference, $30 < \triangle T < 65$℃ ; filling %, 65% ; growth method, vertical temperature gradient method. Under these conditions, morphologies of grown single crystals tended to be bounded by (100), (011) and (201) faces. And the growth rates along the c and b axes were higher than that of the a axis. On the other hand, the IR spectra of the hydrothermally grown KTP single crystals are characterized by absorptions at around 2.7 and 6.2 μm due to the hydroxyl groups. These results are of interest because of the influence of the hydroxyl groups on the nonlinear optical properties such as laser damage threshold, nonlinear optical coefficient, etc.

Acknowledgements

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