

Growth of organic single crystals of L-arginine phosphate monohydrate and tris(hydroxymethyl)aminomethane sulfate

Chang - Sung Lim and Pan - Chae Kim*

Dept. of Material Chemical Engineering, Chonnam National Univ., Kwangju 500- 757, Korea

**Dept. of Inorganic Materials Engineering, Dongshin Univ., Naju 520- 714, Korea*

L-arginine phosphate monohydrate와 tris(hydroxymethyl)-aminomethane sulfate 유기 단결정의 육성

임창성, 김판채*

전남대학교 물질화학공학과, 광주 500-757

*동신대학교 무기재료공학과, 나주 520-714

Abstract L-arginine phosphate monohydrate (LAP) and tris(hydroxymethyl)aminomethane sulfate (THAMS) are new organic nonlinear optical materials for the device application such as the frequency conversion of laser radiation. In this work the single crystals of LAP and THAMS have been grown by the falling temperature method and the temperature difference method. The conditions of the growth parameters were presented and the grown crystals were characterized by means of optical microscopy, XRD and FTIR.

요약 L-arginine phosphate monohydrate (LAP)와 tris(hydroxymethyl)aminomethane sulfate (THAMS)는 레이저의 파장변환소자등과 같은 소자응용에 있어서 새로운 유기 비선형광학재료이다. 본 연구에서는 온도강하법과 온도차법을 이용하여 LAP와 THAMS 단결정의 육성을 시도하였으며 이들 방법에 따른 육성조건을 확립하였다. 그리고 육성결정의 특성을 광학현미경, XRD, FTIR 등을 통하여 평가하였다.

1. Introduction

The frequency conversion of laser radiation in nonlinear optical crystals has become an im-

portant technique widely used in quantum electronics and laser physics for solving various scientific and engineering problems [1]. Organic crystals of L-arginine phosphate

monohydrate (LAP) and tris(hydroxymethyl)-aminomethane sulfate (THAMS) are new nonlinear optical crystals for high-power lasers. Generally nonlinear organic materials have high nonlinear coefficients and high damage threshold. These properties have enabled the production of the various harmonic generators, sum and difference frequency generators, and parametric oscillators [2]. Many of these delocalized π -electron system (consisting of donor and acceptor groups) exhibit nonlinear susceptibilities that are orders of magnitude larger than in most inorganic materials, and they have high optical damage threshold [3].

From a practical point of view, those fields above have stimulated both the development of nonlinear optical materials and the crystal growth of organic materials, since optical quality single crystals are required for applications. LAP is nearly three times more nonlinear than KDP, is somewhat more angularly sensitive, and its damage threshold is two to three times higher and is less deliquescent when compared to KDP. Because of superior properties, these organic single crystals are expected to replace inorganic single crystals, especially in the laser programme [4-6]. These organic single crystals have been prepared by growing usually from solutions. The chemical formula of LAP is $(\text{NH}_2)_2^+\text{CNH}(\text{CH}_2)_3\text{CH}(\text{NH}_3)^+\text{COO}^- \cdot \text{H}_2\text{PO}_4^- \cdot \text{H}_2\text{O}$, which was first reported in 1983 by Xu and coworkers in China [7], while in the case of THAMS, whose chemical formula is $[\text{NH}_2\text{C}(\text{CH}_2\text{OH})_3]_3 \cdot \text{H}_2\text{SO}_4$, the conditions of the crystal growth have not been reported. In this paper we describe the growth of LAP and THAMS crystals from aqueous solution associated with various conditions and the characterizations of the grown

crystals are discussed by means of optical microscopy, XRD and FTIR.

2. Experimental

Organic single crystals of LAP and THAMS were grown from a mixed solution of acid and ionized water by the lowering temperature method and the temperature difference method. The crystallizations from solution in water or organic solvent have long been standard methods for growing large pure crystals of inorganic and organic substances [8].

The starting materials were high purity L-arginine (Junsei Chemical Co. GR Grade) and orthophosphoric acid for the aqueous solution of LAP, and THAM (Junsei Chemical Co., GR Grade) and sulphoric acid for the solution of THAMS. The solutions were prepared by dissolving equimolar L-arginine and orthophosphoric acid, and THAM and sulphoric acid in distilled water. Small seed crystals were prepared by slow recrystallization in a supersaturated solution of mixed solutions and distilled water at temperature ranges from 70°C to 40°C. Solubilities of the seed crystals in aqueous solution were measured at temperatures between 20°C and 40°C by the weight method. According to the solubility data saturated solutions were prepared. The carefully selected seed crystals are hanged to the top of the system.

The seed crystals were immersed in the saturated solutions of the given substances and those crystal growths were regulated by a careful control of the temperature, concentration and degree of agitation of the system. Slow rotation of a magnetic bar in the vessel gives an

adequate movement of the solution around the crystals, and the degree of supersaturation produces crystal growth. The identification of the grown crystals were measured by XRD. The crystal properties and morphologies were observed by means of optical microscopy, XRD and FTIR.

3. Results and discussion

The mole-ratio of L-arginine and orthophosphoric acid for the solution of LAP was 1 : 1, and the mole-ratio of THAM and sulphoric acid for the solution was 3:1. Solubilities in aqueous solution of LAP and THAMS at temperatures between 20°C and 40°C were determined by the weight method. The solubility data of LAP has been already reported with a positive slope at temperatures between 25°C and 43°C [4]. In case of THAMS, the solubility as a function of temperature in aqueous solution are shown in Fig. 1. In both cases, the solubilities of LAP and THAMS have a positive temperature coefficient. The indicated features

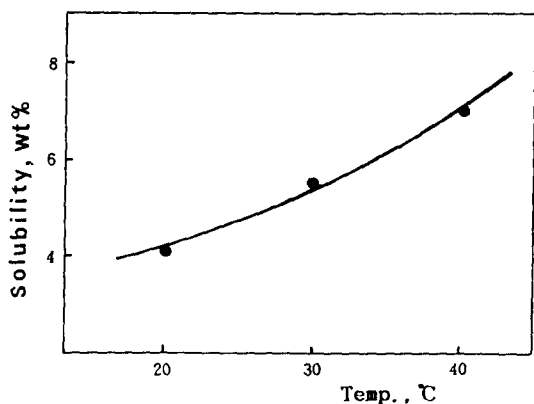


Fig. 1. Solubility of THAMS as a function of temperature in aqueous solution.

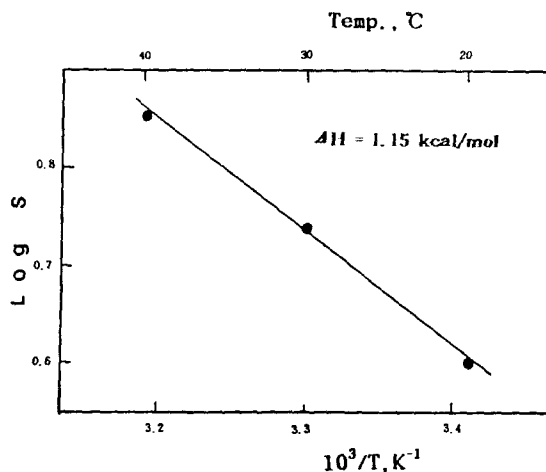


Fig. 2. Log solubility (Log S) of THAMS vs reciprocal temperature in aqueous solution.

of a solubility data provided a suitable crystal growth process in supersaturation solution and led to the nucleation by the temperature differences. The LAP and THAMS particles as a nutrient were placed in a high temperature zone, while the seed crystals were in a low temperature zone. With this arrangement, it was expected that the dissolved nutrient would be used to grow LAP and THAMS single crystals on the seed without occurring of a spontaneous nucleation. The dissolution behavior of THAMS in aqueous solution depends on approximately linearly on temperature and obeys the van't Hoff equation as shown in Fig. 2. In accordance with the log solubility vs $1/T$ of THAMS, we estimate the heat of solution to be $\Delta H = 1.15$ kcal/mol. This heat of solution is lower than those found for KDP single crystals, which are of the order of 3 kcal/mol at higher temperatures between 20°C and 80°C [9].

According to the solubility measurement, seed crystals were obtained by slow recrystallization in a supersaturation solution of the mixed

solutions at temperature ranges from 70°C to 40°C. For seeding processes, the small transparent single crystals, free of macrodefects were obtained at a low part of the solution and selected as the initial seeding crystals by spontaneous crystallizing. The nucleation process was varied according to the crystallizing substance and solvent. The degree of supersaturation lead to ensure a constant rate of growth on the crystal seed.

Based on the solubility measurement and growth processes, large crystals of LAP could be grown at temperatures between 40°C and 45°C with temperature gradients of $\Delta T = 3^\circ\text{C} \sim 4^\circ\text{C}$, and THAMS could be grown at temperatures between 29°C and 31°C with temperature gradients of $\Delta T = 2^\circ\text{C} \sim 3^\circ\text{C}$. Under the conditions LAP crystals of dimension $32 \times 22 \times 15 \text{ mm}^3$ and THAMS crystals with dimensions of $34 \times 20 \times 12 \text{ mm}^3$ could be obtained. The typical crystals of LAP and THAMS are demonstrated in Fig. 3 and Fig. 4. The crystals were grown at a rate of approximately 1.2 mm/day for LAP and THAMS under the conditions. The seed crystal at temperature T could be grown because the solution is nearly saturated at $T + \Delta T$.

The quality and the growth kinetics of crystals grown from solution are influenced by pH of the solution. The pH value of LAP solution was in range 4 to 5, while THAMS solution showed the pH range from 12 to 14. The property of the variation of solubility with pH could be exploited in growing LAP and THAMS single crystals. The presence of excess ions of the stoichiometric pH was responsible for the increase in solubility.

Crystallinities for both crystals of LAP and THAMS under those conditions were identified

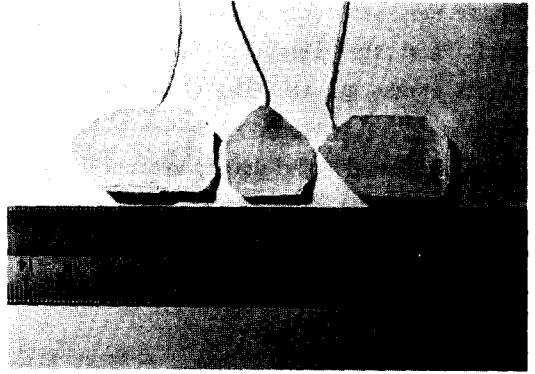


Fig. 3. Typical LAP single crystals grown from aqueous solution by seeded growth.

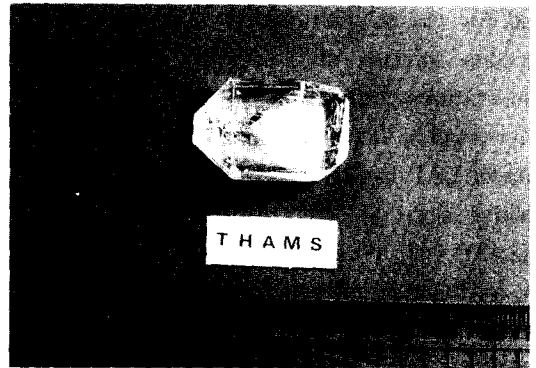


Fig. 4. Typical THAMS crystal grown from aqueous solution by seeded growth.

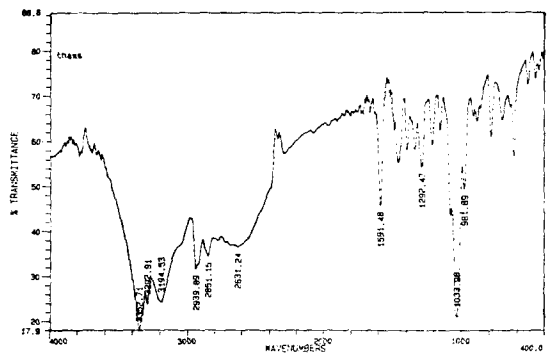


Fig. 5. Infrared spectra of the grown single crystal of LAP.

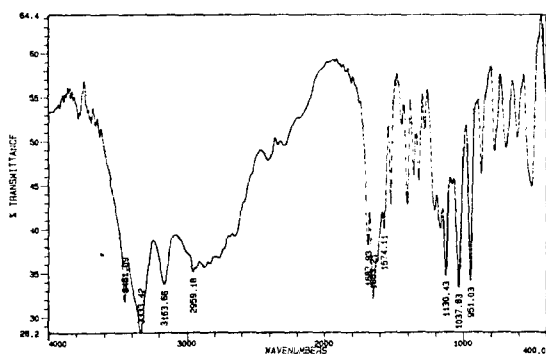


Fig. 6. Infrared spectra of the grown single crystal of THAMS.

by XRD. Typical molecular conformations of both crystallines were characterized by FTIR in Fig. 5 and Fig. 6, which revealed demonstrated transmittances as a function of wavenumbers in ranges between 4000 cm^{-1} and 400 cm^{-1} . As to the spectral characteristics of LAP in Fig. 5, the strong band splittings between 3451 cm^{-1} and 3164 cm^{-1} are caused by the NH stretching mode and the OH stretching modes. The CH stretching modes split into several components at 2959 cm^{-1} . The three tight band splittings at 1600 cm^{-1} are associated with the C(=O)O functional group. The sharp three band splittings at 1000 cm^{-1} exhibit the twisting and wagging mode characteristics of methylen group. In the case of THAMS in Fig. 6, the NH stretching mode and the OH stretching modes give rise to the three strong band splittings at ranges 3353 cm^{-1} and 3194 cm^{-1} , and the CH stretching modes appear in another pair of bands between 2940 cm^{-1} and 2631 cm^{-1} . The sharp bands at 1591 cm^{-1} , 1292 cm^{-1} and 1034 cm^{-1} are due to the NH bending mode, the S=O functional group and the CH wagging mode, respectively.

4. Conclusions

Single crystals of LAP and THAMS were grown from aqueous solution by the lowering temperature method and the temperature difference method at different growth conditions. The mole-ratio of L-arginine and orthophosphoric acid for the solution of LAP was 1:1, and the mole-ratio of THAM and sulphoric acid for the solution was 3:1. The solubilities of LAP and THAMS have a positive temperature coefficient. The heat of solution of THAMS was estimated to be $\Delta H = 1.15\text{ kcal/mol}$, which is lower than the value of KDP. Large crystals of LAP were grown at temperatures between 40°C and 45°C with temperature gradients of $\Delta T = 3^\circ\text{C} \sim 4^\circ\text{C}$, while THAMS were grown at temperatures between 29°C and 31°C with temperature gradients of $\Delta T = 2^\circ\text{C} \sim 3^\circ\text{C}$. The growth rate was estimated to be approximately 1.2 mm/day for both crystals under the conditions. The pH value of LAP solution was in range 4 to 5, and THAMS solution showed the pH range from 12 to 14. Typical band splittings of both crystals by infrared spectra were due to the several kinds of stretching, wagging and bending modes of NH, OH and CH, and a few functional groups.

LAP and THAMS single crystals are very interesting as a laser frequency converting materials. More investigations in the field of crystal growth and characterizations are required for the applications. Details about those investigations of crystal growth and optical properties of these crystals and other organic nonlinear optical crystals will be presented in another paper.

References

- [1] V.G. Dmitriv, G.G. Gurzadyan and D.N. Nikogosyan, Handbook of Nonlinear Optical Crystals, Springer Series in Optical Sciences, Vol. 64 (1990).
- [2] Y. Kitaoka, T. Sasaki, S. Nakai and Y. Goto, Appl. Phys. Lett. 59 (1991) 19.
- [3] N. Zhang, D. Yuan, X. Tao, Z. Shao, S. Dou, M. Jiang and D. Xu, J. of Crystal Growth 123 (1992) 255.
- [4] G. Dhanaraj, T. Shripathi and H. L. Bhat, J. of Crystal Growth 11 (1991) 456.
- [5] A. Yokotani, T. Sasaki, K. Fujioka, S. Nakai and C. Yamanaka, J. of Crystal Growth 99 (1990) 815.
- [6] A. Yokotani, T. Sasaki, K. Yoshida and S. Nakai, Appl. Phys. Lett. 55 (1989) 2692.
- [7] D. Xu, M. Jiang and Z. Tan, Acta Chemica Sinica 41 (1983) 570.
- [8] J.C. Brice, Crystal Growth Process, (John Wiley and Sons Inc., New York, 1986) p. 167.
- [9] P.C. Kim, K.R. Choi, J. of Kor. Assoc Crystal Growth 2 (1992) 37.