Cryst. Res. Technol. **40**, No. 9, 867 – 870 (2005) / **DOI** 10.1002/crat.200410447

Rapid growth of KDP crystal from aqueous solutions with additives and its optical studies

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Received 15 September 2004, accepted 2 December 2004
Published online 15 August 2005

Key words KDP crystal, rapid growth, KCl; EDTA, optical properties.
PACS 81.10.Dn

Potassium Chloride (KCl) and Ethylene diamine tetraacetie acid (EDTA) as new additives were added into the KDP solutions in a small amount (5M% and 0.01M% respectively). The solubility curve and metastable zone width of KDP solution with 5M%KCl was determined and we explained the mechanism of rapid growth of KDP crystal with KCl additve. The clear transparent crystal of KDP with a dimension of 54×54×42mm have been grown rapidly by cooling solution method in 2 days. The crystal grown from additives added solution was subjected to optical transmission and laser damage threshold studies as compared with the crystal grown by traditional growing method.

1 Introduction

The very high-energy lasers used for inertial confinement fusion research, need large plates of nonlinear potassium dihydrogen orthophosphate (KDP) crystals for electro-optic switches and frequency converters. The approximately 40×40 cm^2 aperture of lasers under construction in the US and France, require single crystal boules with linear dimensions in the 50-100 cm range [1]. The growth rate of such large crystals by traditional techniques is merely 0.5-1 mm/day typical for low-temperature solution growth. Slow growth leads to growth cycles exceeding one-two years. The difficulties in providing reliable equipment, the high risk of failure, and defect formation during such long periods result in low yield and high cost of the final crystals. These reasons stimulated the development of new techniques to accelerate the growth without sacrificing optical quality of large crystals.

Zaitseva et al. of LLNL grew large-scale (40-55 cm) KDP crystals at rates of 10-20 mm/d, the rapid growth method is based on the use of "point seed" [2]. Nakatsuka et al. used external energy to grow KDP crystals of 60 mm in size at high rates of excess of 50 mm/d [3]. However, these new techniques above require raw material of higher purity, acoustic power and continuous filtration system.

The adjustment effect of additives on the growth process and properties of crystals has been applied in recent years [4-8]. With additives, KDP crystals can be grown rapidly in the traditional crystallizers of simple design for conventional growth. In this present work, KDP crystals were grown from the aqueous solutions added with 5M% KCl and 0.01M% EDTA, J. Podder [9] reported that the presence of KCl in the growth medium is also found to suppress the metal ion impurities to a large extent and increases the growth rate. The increase in the quality of the KDP crystal in presence of KCl is due to the complexation of trace metal ion impurities in solution by Cl ion. These complex metal impurities cannot get into the crystal lattice. In our experiments, we found that the addition of EDTA can improve the quality of crystal with highest transparency, so we choosed KCl and EDTA as additives. The solubility curve and metastable zone width of 5M% KCl added solution is also measured comparing to the pure system. Grown crystals were subjected to optical transmission and laser damage threshold studies.

2 Experimental

2.1 Solubility curve and determination of metastable zone width

The solubility curve was measured by means of traditional weight analysis, and we could also measure the avalanche point temperature by watching the appearance of spontaneous crystallization of solutions. The

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solution was filtered through a 0.15μm membrane and kept in a 5000ml vessel with a seed hold rotating in the mode of "forward-stop-backward" with a speed of 30 rpm. The solutions were stirred for about 24 h continuously for stabilization and slowly cooled at a desired cooling rate of 4K/h. The metastable region was shown in Fig. 1. The solubility curve of pure KDP solution was adopted from report by Yang Shangfeng et al. [4] which is measured by means of traditional weight analysis.

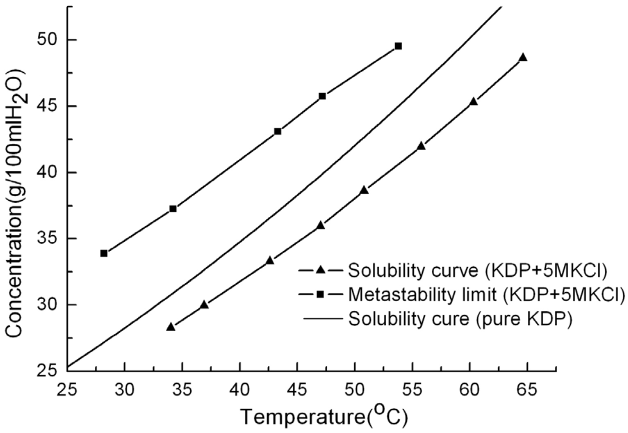

Fig. 1 Solubility curve and metastability limit curves of pure and KCl added KDP solutions.

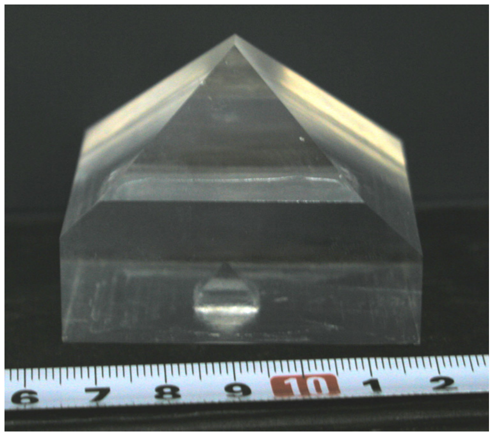

Fig. 2 Photograph of the grown KDP crystal (reflection of fluorescent lamp light in two pyramid faces).

In our experiments we found that when 5M%KCl was added into the solution and dissolved because of small amount of KCl in water, the temperature of KDP crystal saturation was raised. So the solubility curve of KDP solution with 5M% KCl is on the right side of the solubility curve of pure KDP solution. The metastable zone width of KDP solution with 5M% KCl was doubled and greatly wider than that of pure KDP solution. It is the reason that the addition of KCl can make KDP solution more stable than other additives and increase grow rate of KDP crystal under higher supercooling. At the same time, addition of KCl enhances the zone width of KDP solution for all the temperatures. In our experiments, we found that the addition of EDTA can improve the quality of crystal with highest transparency, so we chose KCl and EDTA as additives.

2.2 Crystal growth

The starting material was KDP pure reagents (G.R., Merck). Pure water by Milli-Q ultrapure water purification system with resistivity of 18.2MΩ·cm was used as the solvent. KCl (G.R.) and EDTA (A.R.) were used as additives.

Table 1 Growth characteristics of KDP crystals.

Saturation temperature	Super-cooling	Period (d) (until the crystal reach the pillars of seed holder)	Spontaneous Crystallization	Size (mm^3) X	Y	Z	Growth rate Rx/Rz(mm/day)
64.10°C	8K	2	none	54	54	42	23/21

All experiments are carried out in a standard glass 5000 ml crystallizer, used for conventional crystal growth by the method of temperature reduction. The temperature of crystallizer is controlled using an external water bath, and the temperature fluctuations are less than ±0.02K. The reversible rotation rate of the platform with the crystal was about 30 rpm. The solutions with 5M% KCl and 0.01M% EDTA are filtered through filters with a pore diameter of 0.15 μm to remove extraneous solid and colloidal particles. After filtration the solutions were overheated at 75ºC for 24h. Then the temperature of solution was reduced to 5K higher than saturation point and then the seed was *Z*-cut with the size of about 8×8×3 mm and placed into the solution. Then we reduced the temperature to a critical value of supercooling and the seed crystal began to grow upwards. The grown crystals were shown in Fig. 2. Growth characteristics of KDP crystal was listed in Table 1.

3 Characterizations

3.1 XRD analysis

The X-ray powder diffraction analysis was used to confirm the physical phase of the product. Grown crystals were ground using an agate mortar and pestle in order to determine the crystal phases by X-ray diffraction. The XRD analysis (Rigaku, D/max-2500) was performed with a graphite-monochromated CuKα radiation using a tube voltage and current of 40 kV and 100 mA, respectively. Table. 2 lists the observed d values and intensity of KDP crystal rapidly grown from 5M% KCl added solution compared with those of pure KDP crystal, χ-ray powder diffraction patterns of the product are consistent with the pure KDP crystal and no other impurities and therefore the additive will not deteriorate the NLO properties.

Table 2 The χ-ray powder diffraction data.

d(1wt% KCl)	d(pure KDP)	I(1wt% KCl)	I(pure KDP)
5.0968	5.1083	weak	weak
3.7296	3.7330	very strong	very strong
3.0985	3.0104	weak	weak
2.9075	2.9103	middle	middle
2.6348	2.6379	weak	weak
2.5414	2.5472	weak	weak
2.3395	2.3415	weak	weak
2.2179	2.2212	weak	weak
1.9810	1.9831	weak	weak
1.9487	1.9531	middle	middle

3.2 Optical transmission studies

Z-cut KDP crystal plates with a size of about 20×20×10.5mm were polished at face (001) without any antireflection coating for optical measurements. Optical transmission spectra were recorded for the samples obtained from pure solution by traditional method as well as 1 wt% of organic compounds KCl added solution by rapid growth method. The spectra were recorded in the wavelength region from 190 to 2100 nm using PE-lambda900 spectrometer. The recorded spectra are shown in Fig 3. This shows that the additives have not destroyed the optical transparency of the crystal. In the UV region, KDP crystal grown from KCl added solution has a higher transparency than the KDP crystal grown from pure solution by traditional method.

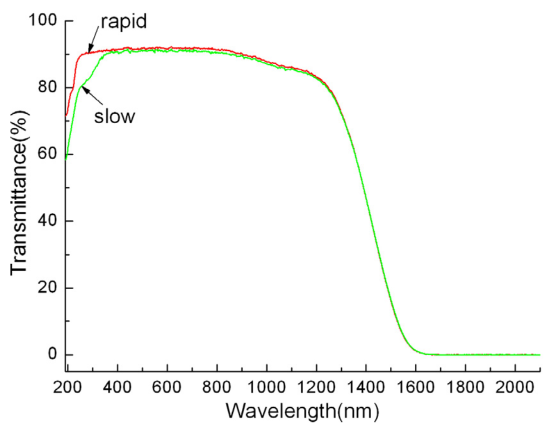

Fig. 3 Transmission spectra of KDP crystals.

3.3 Laser damage threshold

The laser damage thresholds were measured with well polished samples obtained in the above experiments. The measurement was carried out in Shanghai Institute of Optics and Fine Mechanics at the conditions of wavelength 1.06 μm, and pulse width 1ns. The results of laser damage threshold measurement are listed in

Table 3. The damage threshold of KDP crystal from KCl added solution was 6.86J/cm^2 and reach to 15.9J/cm^2 after annealing at 423K for 20h which can meet the need of the Inertial Confinement Fusion (ICF).

Table 3 The comparison of damage threshold.

Sample	wavelength	pulse width	Threshold (J/cm^2)
KDP(before annealing)	1064nm	10ns	6.86
KDP(after annealing)	1064nm	10ns	15.9

4 Conclusion

The metastable zone width of KDP solutions in their supersaturated region is found enhanced greatly by the incorporation of 5M% KCl and 0.01M% EDTA. The addition of KCl can make KDP solution more stable than other additives and increase grow rate of KDP crystal under higher supercooling. The addition of EDTA can just improve the quality of crystal with highest transparency. The KDP crystal grown from KCl added solution in a standard 5000ml vessel has a size of 54×54×42mm and the growth rate is more than 20mm/day. The X-ray curves recorded for the crystals grown from 5 M% KCl added solutions proved that this KCl incorporation does not affect the crystalline perfection and its quality. The optical transparency and the laser damage threshold after annealing at 423K of rapidly grown crystal are as good as those of the crystal of high quality grown by traditional method.

Acknowledgements The financial support of this work is provided by the State High Technology Program for Inertial Confinement Fusion (Project 863-416-2) and Fujian Provincial Natural Science Fund (E0216630) which is gratefully acknowledged.

References

[1] N. Zaitseva and L. Carman, Prog. Cryst. Growth Charact. **43,** 118 (2001).
[2] N. P. Zaitseva, J. J. De Yoreo, M. R. Dehaven, R. L. Vital, K. E. Montgomery, M. Richardson, and L. J. Atherton, J. Cryst. Growth **180**, 255 (1997).
[3] M. Nakatsuka, K. Fujioka, T. Kanabe, and H. Fujita, J. Cryst. Growth **171**, 531 (1997).
[4] Yang Shangfeng, Su Genbo, Li Zhengdong, and Jiang Rihong, J. Cryst. Growth **197,** 383 (1999).
[5] T. Sasaki and A. Yokotani, J. Cryst. Growth **99**, 820 (1990).
[6] A. Yokotani, H. Koide, T. Sasaki, and T. Yamanaka, J. Cryst. Growth **67,** 627 (1984).
[7] B. Dam, P. Bennema, and W. J. P. Van Enckevort, J. Cryst. Growth **74**, 118 (1986).
[8] S. L. Wang, Z. S. Gao, Y. J. Fu, A. D. Duan, X. Sun, C. S. Fang, and X. Q. Wang, Cryst. Res. Technol. **38**, 941 (2003).
[9] X. Sun, Z. P. Wang, S. L. Wang, Q. T. Gu, X. G. Xu, Y. P. Li, and C. S. Fang, Cryst. Res. Technol. **39**, 796 (2004).
[10] Kouji Maeda, Akira Sonoda, Hideo Miki, Yusuke Asakuma, and Keisuke Fukui, Cryst. Res. Technol. **39**, 1006 (2004).