

# Study on optical property of rapid growth KDP and DKDP crystals

Mingxia Xu, Zhengping Wang, Bo Wang, Baoan Liu, Xun Sun, Xinguang Xu  
(State Key Laboratory of Crystal Materials, Shandong University, Jinan, 250100)

**Abstract:** In this paper, DKDP with deuterium content of 60% and KDP crystals were grown by “point-seed” rapid growth method. Optical property including transmittance spectra, conoscopic image, light scattering and laser damage threshold (LDT) were measured. The results showed that although the infrared absorption edge of transmission spectra is obviously red-shifted, structure perfection and optical homogeneity of DKDP crystal became poorer. Light scattering have no obvious change. We also found that the value of LDT at 1064 nm has a 2.5-3.8× increase compared with that tested at 532 nm and LDT of Z-cut samples is obviously higher than that of tripler-cut samples.

**Key words:** KDP and DKDP crystals; “point-seed” rapid growth; optical property

## 0 Introduction

Potassium dihydrogen phosphate (KDP) and its deuterated analog DKDP are two of the most important nonlinear materials and the only one that can be grown to very large size<sup>[1]</sup>. In the third harmonic generation (THG) of Nd:glass laser, DKDP is preferred used to substitute KDP crystal for its weak stimulated Raman scattering (SRS) effect<sup>[2-3]</sup>. However, for the traditional temperature-reduction method of DKDP crystal growth, the growth rate is merely 0.5-1 mm/day which leads to growth cycles exceeding 1-2 years. During such long periods, the high risk of failure and defect formation will result in low yield and high cost of the final crystals. These reasons stimulated the development of the rapid growth technique of KDP and DKDP crystals<sup>[4, 5]</sup>.

In recent years, people have more interest in rapid growth of KDP and DKDP crystals and improving its quality. Chernov et al. used “point-seed” technique to grow DKDP crystal with the growth rate of 40~25 mm/day and 20~25 mm/day for [001] direction and [100] direction, respectively in 1990<sup>[6]</sup>. Zaitseva et al. grew high deuterium-content DKDP crystals of 516 mm in size at a rate of 10~40 mm/day in 1995<sup>[7]</sup>. In 1997, Zaitseva et al. also grew large-scale (40~50cm) KDP crystal at a rate of 10~20 mm/d by rapid growth technique<sup>[8]</sup>. In the same year, Nakatsuka et al. used external energy to grow KDP crystal of 60 mm in size at high rate of excess of 50 mm/day<sup>[9]</sup>. Additionally, in 1999, Zaitseva et al. successfully designed a continuous filtration system to improve the purity of growth solution and got KDP and DKDP crystals with linear dimension in the 50-55 cm range at a growth rate of 12-15 mm/day which have low dislocation density, high optical homogenization and high laser damage threshold<sup>[10]</sup>.

In this paper, DKDP and KDP crystals were grown by “point seed” technique. We studied the optical property of KDP and DKDP crystals.

## 1 Experimental

### 1.1 Crystal growth & sample preparation

DKDP crystal was grown from aqueous solution by using the “point seed” technique in a

---

Foundations: Doctoral Program Foundation of Institutions of Higher Education of China (No.20090131120035)  
Brief author introduction: Mingxia XU(1984-), Female, The growth of KDP crystal  
Correspondance author: Xun Sun(1972-), Male, Professor, Study on the growth of KDP crystal. E-mail: sunxun@icm.sdu.edu.cn

40 standard glass 5000ml crystallizer. The D content of growth solution is around 70%, which can get DKDP crystal with the D content of 60%<sup>[11]</sup>. Crystallization was performed in a temperature range 56.2-53.5°C for DKDP (crystal B) and 56.9-53.2°C for KDP (crystal A) using the same raw material under the similar growth conditions. The velocity of crystal growth in Z axis is 6-7mm/day. The crystal rotated in the mode of “forward-stop-backward” with a speed about 77 rpm. The as-grown crystals were shown in Fig. 1

45 Two Z-cut crystal plates which belong to the prism sectors and two type-II tripling-cut crystal plates which belong to the pyramidal sectors of crystal A and B, designated as samples A1, A2, B1 and B2 in Fig.2, respectively, were oriented by X-ray diffraction and polished thoroughly with a thickness of 9 mm for A1, B1 and 10mm for A2, B2.

50

(a) Crystal A (KDP) (b) Crystal B (DKDP)

Fig. 1 Photographs of crystals grown by point-seed rapid growth method

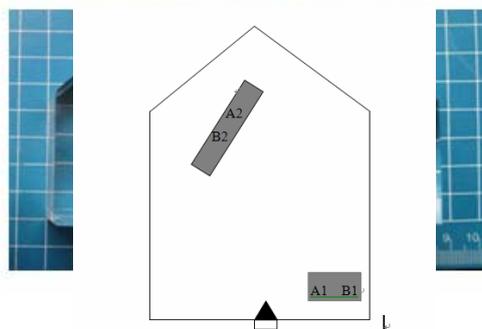


Fig. 2 Photographs of angular orientation of crystals samples

## 55 1.2 Structure measurement

High-resolution X-ray diffractometer (HRXRD) was used to study the crystalline perfection of the grown crystals<sup>[12]</sup>. Sample A1 and sample B1 were tested by HRXRD (D5005HR, Bruker AXS) in our measurement which was performed using the voltage and current of 30KV and 30mA, respectively.

60 Lattice constant was measured by X-Ray Single Crystal Diffractometer (Smart APEX II, Bruker).

## 1.3 Optical property measurement

The transmittance spectra of the crystals were measured by a spectrophotometer (Model U-3500, Hitachi) in the range of 200–2000 nm.

65 Conoscopic image was used to study the homogeneity of the crystals which was observed using 532nm laser as a light source.

Ultra-microscopy which has been widely used in detecting defects of crystals was used to investigate the scattering centers in the crystals using the laser of 532nm<sup>[13]</sup>.

70 The damage performance was evaluated by measuring the scatter of damage pinpoint in crystal. The fundamental and second harmonics of the output of a Q-switched Nd:YAG laser were focused by a lens with  $f=500$  mm into the material. The pulse width of 1064nm, 532nm (full-width of half-maximum, Gaussian shapes) is 18ns, 15ns respectively. The laser ran at a repetition rate of 1 Hz. For  $1\omega$  and  $2\omega$  waves, the spot areas of the laser beam were  $0.18\text{ mm}^2$ ,  $0.25\text{ mm}^2$  respectively.

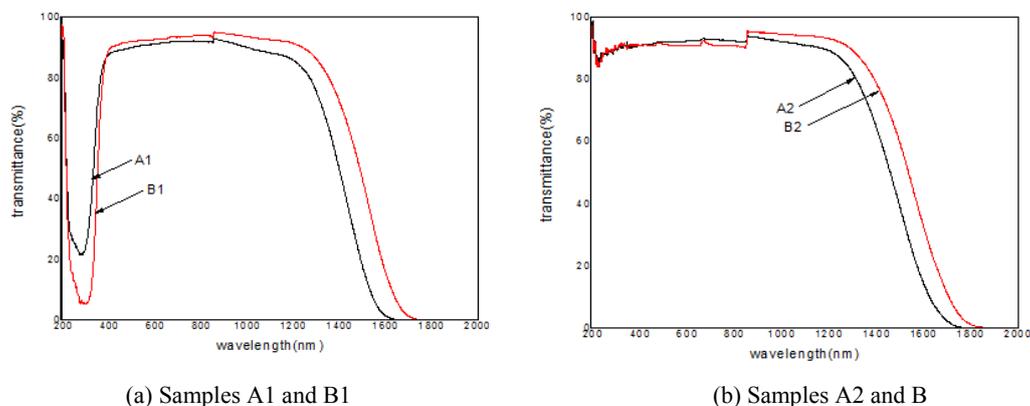
## 75 2 Results and discussion

### 2.1 Optical transmission

The transmission spectra of four crystal samples are shown in Fig.3. The infrared absorption edge of the DKDP crystal is obviously red-shifted in comparison to that of the KDP crystal so that the DKDP crystal can be applied in wider wavelength region. Comparing Fig.3 (a) with Fig.3 (b), the transmittance of samples A2 and B2 is higher than that of samples A1 and B1 in the ultraviolet region. This might have been due to the difference of structural characteristics in the crystals; for example, trivalent metallic ionic impurity (such as  $\text{Fe}^{3+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Al}^{3+}$ ) tends to exist in the prism sector of the crystal<sup>[14]</sup>. As we know, highly-charged metallic ionic impurity has a complex energy level and the rich spectra. It can easily cause strong absorption in the ultraviolet region. Additionally, the absorption of defects in the ultraviolet region will also lead to the deterioration of the transmission spectra.

As seen from Fig.3 (a), the transmittance of sample B1 is slightly higher than that of sample A1 in the range of 400-1800nm while the transmission of sample A1 has a lower optical absorption ratio than that of sample B1 in the ultraviolet region. The transmittance of sample B1 falls to about 15% compared with that of A1.

Fig.3 (b) shows that the infrared absorption edge of the tripler cut samples is obviously red-shifted in comparison to that of the Z-cut samples. It demonstrates that the slice type has an influence on the transmission spectra.



95 (a) Samples A1 and B1 (b) Samples A2 and B  
Fig. 3 Transmission spectra of the KDP and DKDP crystals (left for Z-cut samples, right for type-II tripling-cut samples)

### 2.2 Conoscopic image

100 Conoscopic image is used to study the optical homogeneity of the crystals. Fig.4 shows that the two crystals A and B have obvious characteristic of single axis and the interference fringes are evenly distributed. It indicates that the optical uniformity of crystals is very good. However, this is only the result gotten from macrostructure of the samples. In order to further study the effect of the D element on the microstructure of the crystal, rocking curves and lattice constant were  
105 measured.

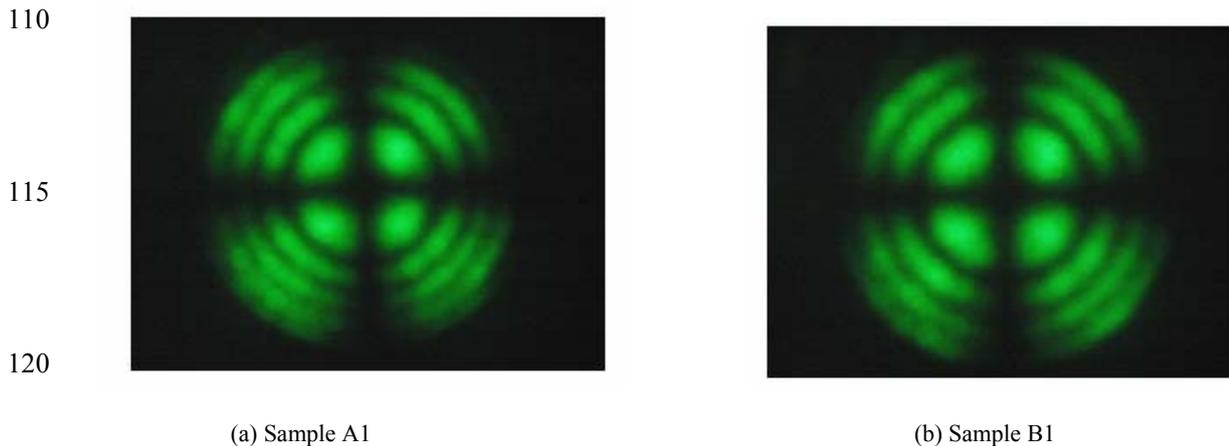


Fig.4 Conoscopic figures of [001] crystal plate sample

Fig. 5 shows the typical high-resolution diffraction curve recorded for the samples A1 and B1. As seen in the figure, the curves are sharp and contain only a single diffraction peak. Absence of additional peaks and very sharp diffraction curves show that the crystalline perfection of the crystals is good. However, the curve of sample A1 is sharper having the full width at half maximum (FWHM) of 15.84 arcsec than that of sample B1 with the FWHM of 19.80 arcsec. It clearly shows that the crystalline perfection of the DKDP crystal is poorer compared to that of KDP crystal. This is due to the hydrogen element in the KDP crystal partly replaced by deuterium element which leads to the lattice distortion. Lattice constant which has been measured are shown in Table 1. From it, we can clearly see that lattice parameter values for DKDP crystal change obviously compared with KDP crystal.

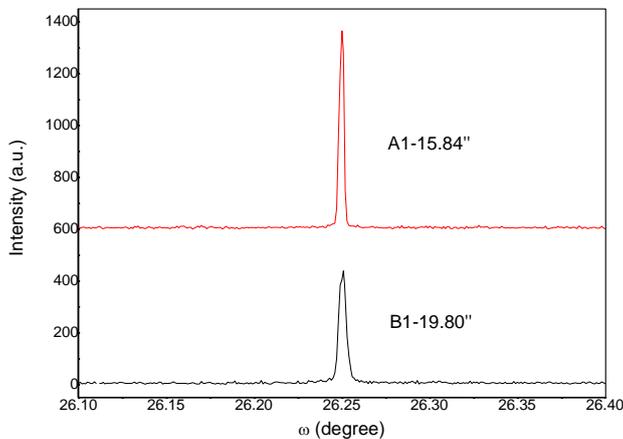


Fig. 5 Rocking curves of HRXRD on sample A1 and sample B1

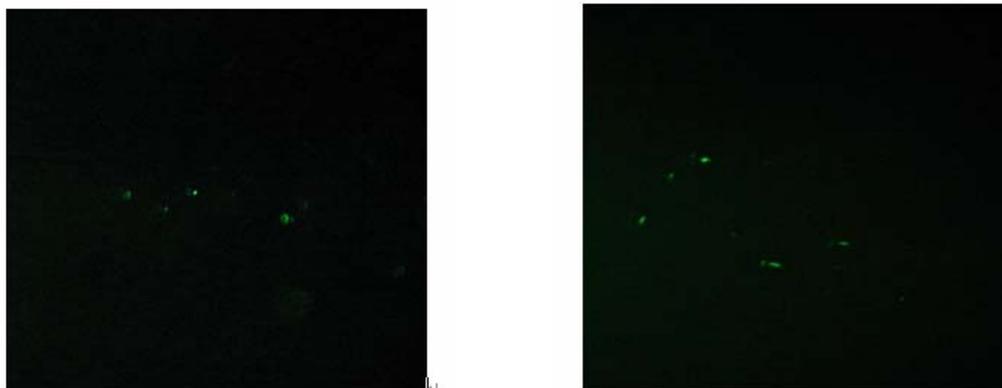
Table 1 Lattice constant for KDP and DKDP crystals

Sample	a (nm)	b (nm)	c (nm)
KDP	0.74507	0.74507	0.69727
DKDP	0.74532	0.74532	0.69944

Thus, the homogeneity of DKDP crystal becomes lower due to the impact of deuterium element. However, the influence of deuterium content to the crystal uniformity is not obvious in our measurement. The results will be further discussed in another paper [to be published].

150 **2.3 Light scattering of the crystals**

Scattering particles is an important parameter for nonlinear optical crystal. The density of scattering particles in the crystal has an influence on the damage threshold [15]. The more scattering particles are in crystal, the lower the damage threshold decreases. This is because the existence of the scattering particles leads to the uneven distribution of the beam energy which makes the laser energy density increasing in some local area of the crystal. This results in the damage happened in the crystal under the lower energy. The morphology of scattering centers in sample A1 and sample B1 are shown in Fig.6. Compared with sample A1, the numbers of the scattering centers do not obviously increase in sample B1. Scattering centers distribute randomly both in crystal A and crystal B.



(a) Sample A1

(b) Sample B1

Fig. 6 Morphology of scattering centers in samples A1 and B1

160 **2.4 Laser induced damage threshold**

Table 2 was the result of laser damage threshold (LDT). From it, we can clearly see that:

(1) In general, LDT of the crystals decrease with the increasing of laser frequency. The value for damage testing at 1064 nm is 2.5-3.8× that for damage testing at 532 nm. This is maybe due to the difference of defect types which caused laser damage of the crystals under the different wavelengths [16]. For shorter wavelength of the laser, the absorption ratio of the crystals is obviously higher which leads to the increase of defect temperature more distinctly so that the damage is more likely to happen in the crystal.

(2) LDT of the Z-cut samples is obviously higher compared with that of the type-II tripling-cut samples for both 1ω and 2ω. It has a strong dependence on the laser propagation direction [17-19]. Fluid-filled inclusions are known to occur in KDP and DKDP with sizes in the

175 micrometer range which are microscopic lenslets. Such inclusions can be ellipsoidal and oriented to a direction so that the absorption of laser will be enhanced in that direction. Moreover, it is also probably caused by the anisotropy of crystals. Samples cutting from various directions of crystals have different property which inevitably leads to the distinction of laser damage threshold.

Tab. 2 Laser damage thresholds of the crystal samples

No.	Laser damage threshold /(J/cm <sup>2</sup> ,1064nm,18ns)	Laser damage threshold /(J/cm <sup>2</sup> ,532nm,15ns)
A1	33.54	9.23
A2	20.21	5.95
B1	23.26	9.16
B2	18.49	4.85

### 180 3 Conclusion

KDP and DKDP crystals were grown using the point-seed rapid grown method. The results indicate that, due to the hydrogen element in the KDP crystal partly replaced by deuterium element, the crystalline perfection and optical homogeneity of DKDP crystal become poorer though the infrared absorption edge of the transmission spectra is obviously red-shifted. The light scattering shows a similar situation in the KDP and DKDP crystals. For KDP and DKDP crystals, the value of laser damage threshold at 1064 nm has a 2.5-3.8× increase compared with that tested at 532 nm and LDT of Z-cut samples is obviously higher than that of the type- II tripling-cut samples whether for 1 $\omega$  or for 2 $\omega$ .

### 4 Acknowledgements

190 This research is supported by Doctoral Program Foundation of Institutions of Higher Education of China (No.20090131120035)

### References

- 195 [1] J.J. De Yoreo, A.K. Burnham, and P.K. Whitman. Developing KH<sub>2</sub>PO<sub>4</sub> crystals for the world's most powerful laser [J]. *Int. Mater. Rev.* 47, 113 (2002).
- [2] S. L. Wang, Z. S. Gao, Y. J. Fu, et al. Study on rapid growth of highly-deuterated DKDP crystals [J]. *Cryst. Res. Technol.* 38, 941 (2003).
- [3] J. H. Campbell, R.T. Maney, L. J. Atherton et al. Large aperture, high damage threshold optics for beamlet [R]. LLNL Report, UCRL-LR-105821-95-1 (1995).
- 200 [4] N. P. Zaitseva, L. Carman. Rapid growth of KDP-type crystals [J]. *Progress in Crystal Growth and Characterization of Materials*, 1-118 (2001).
- [5] X. Sun, X. G. Xu, Z. P. Wang, S. L. Wang, et al. Study on the optical properties of rapidly grown KDP crystals [J]. *Journal of Synthetic Crystal*, 31, 440-444 (2002).
- 205 [6] N. P. Zaitseva, L. N. Rashkovich. Secondary nucleation induced by the cracking of a growth crystal: KH<sub>2</sub>PO<sub>4</sub> (KDP) and K (H, D) PO<sub>4</sub> (DKDP) [J]. *J. Cryst. Growth*, 102, 793-800 (1990).
- [7] N. P. Zaitseva, L. N. Rashkovich, S. V. Bogatyreva. Stability of KH<sub>2</sub> PO<sub>4</sub> and K (H, D) 2 PO<sub>4</sub> Solutions at Fast Crystal Growth Rates [J]. *J. Cryst. Growth*, 148, 276-282 (1995).
- [8] N. P. Zaitseva, J. J. De Yoreo. Rapid Growth of Large-scale (40-55 cm) KH<sub>2</sub> PO<sub>4</sub> Crystal [J]. *J. Cryst. Growth*, 180, 255-262 (1997).
- 210 [9] M. Nakatsuka, K. Fujioka, T. Kanabe, et al. Rapid growth over 50 mm/day of water-soluble KDP crystal [J]. *J. Cryst. Growth*, 171, 531 (1997).
- [10] N. P. Zaitseva, J. Atherton, R. Rozsa, L. Carman, I. Smolsky, M. Runkel, R. Ryon, L. James. Design and Benefits of Continuous Filtration in Rapid Growth of Large KDP and DKDP Crystals [J]. *J. Cryst. Growth*, 197, 911 (1999).

- 215 [11] G. M. Loiacono, J. F. Balascio, W. Osborne. Effect of deuteration on the ferroelectric transition temperature and the distribution coefficient of deuterium in K (H<sub>1-x</sub>D<sub>x</sub>)<sub>2</sub>PO<sub>4</sub> [J]. Appl. Phys. Lett. 24, 455 (1974).  
[12] P.V.Dhanaraj, C.K.Mahadevan, et al. Growth and characterization of KDP crystals with potassium carbonate as additive [J]. J. Cryst. Growth, 310, 1-6 (2008).
- 220 [13] X. Sun, X. G. Xu, Z. S. Gao, Y. J. Fu, S. L. Wang, H. Zeng, Y. P. Li. Effect of EDTA on the light scatter in KDP crystal [J]. J. Cryst. Growth, 217, 404-409 (2000).  
[14] E. Dieguez, A. Cintas, P. Hernandez, et al. Ultraviolet absorption and growth bands in KDP [J]. J. Cryst. Growth, 73, 193-195 (1985).  
[15] B. Woods, M. Runkel, M. Yan, et al. Investigation of damage in KDP using light scattering techniques [R]. LLNL Report, UCRL-JC-125368 (1997).
- 225 [16] S. T. Sun. Study on the growth and improving laser induced damage threshold of DKDP crystals [D]. Jinan: Shandong University, 2010.  
[17] Alan K. Burnham, Michael Runkel, Michael D. Feit, Alexander M. Rubenchik, et al. Laser-Induced Damage in Deuterated Potassium Dihydrogen Phosphate [J]. Appl. Opt., 42, 5483-5495 (2003).
- 230 [18] H. Yoshida, T. Jitsuno, H. Fujita, et al. Investigation of bulk laser damage in KDP crystal as a function of laser irradiation direction, polarization, and wavelength [J]. Appl. Phys. B, 70, 195-201 (2000).  
[19] G. H. Hu, Y. A. Zhao, S. T. Sun, et al. One-on-One and R-on-One Tests on KDP and DKDP Crystals with Different Orientations [J]. CHIN. PHYS. LETT., 26, 087801-1 (2009).

## 235 快速生长的 KDP 和 DKDP 晶体光学性质的研究

徐明霞, 王正平, 王波, 刘宝安, 孙洵, 许心光  
(山东大学晶体材料国家重点实验室, 济南 250100)

240 **摘要:** 本文采用“点籽晶”快速生长法生长了 KDP 晶体和晶体含氘量为 60% 的 DKDP 晶体, 测量了其透过光谱、锥光干涉、散射颗粒及损伤阈值等光学性质。实验结果表明: 虽然 DKDP 晶体透过光谱的红外截止边发生明显红移, 但是其晶体结构的完整性和光学均匀性变差, 而散射颗粒没有明显变化。KDP 和 DKDP 晶体基频光损伤阈值是倍频的 2.5-3.8 倍, 其 Z 切样品的损伤阈值明显高于三倍频切片。

245 **关键词:** KDP 和 DKDP 晶体; “点籽晶”快速生长; 光学性质  
**中图分类号:** O781