Study on optical property of rapid growth KDP and DKDP crystals

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Potassium dideuterium phosphate (DKDP) with deuterium content of 60% and potassium dihydrogen phoshate (KDP) crystals are grown by "point-seed" rapid growth method. Optical property including transmittance spectra, conoscopic image, light scattering and laser damage threshold (LDT) are measured. The results show 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 find that the value of LDT at 1 053 nm has a 2.5-3.8× increase compared with that tested at 526 nm and LDT of Z-cut samples is obviously higher than that of tripler-cut samples.

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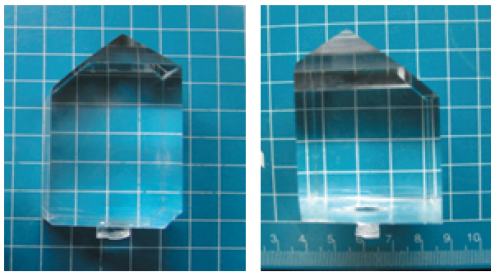
Potassium dihydrogen phosphate (KDP) and its deuterated analog potassium dideuterium phosphate (DKDP) are two of the most important nonlinear materials and the only one that can be grown to very large size[1]. In the third harmonic generation (THG) of Nd:glass laser, DKDP is preferred used to substitute KDP crystal for its weak stimulated Raman scattering (SRS) effect[2−3]. 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[4,5].

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[6]. Zaitseva *et al.* grew high deuterium-content DKDP crystals of 516 mm in size at a rate of 10∼40 mm/day in 1995[7]. In 1997, Zaitseva *et al.* also grew large-scale (40∼50 cm) KDP crystal at a rate of 10∼20 mm/d by rapid growth technique[8]. 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[9]. 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[10].

In this letter, DKDP and KDP crystals are grown by "point seed" technique. We study the optical property of KDP and DKDP crystals.

DKDP crystal was grown from aqueous solution by using the "point seed" technique in a standard glass 5 000-mL crystallizer. The D content of growth solution is around 70%, which can get DKDP crystal with the D content of 60%[11]. Crystallization was performed in a temperature range of 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 6-7 mm/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.

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,



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

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

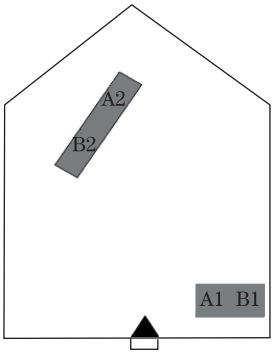


Fig. 2. Photographs of angular orientation of crystals samples.

respectively, were oriented by X-ray diffraction and polished thoroughly with a thickness of 9 mm for A1, B1 and 10 mm for A2, B2.

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

Lattice constant was measured by X-Ray Single Crystal Diffractometor (Smart APEX II, Bruker, Germany). The transmittance spectra of the crystals were measured by a spectrophotometer (Model U–3500, Hitachi, Japan) in the range of 200-2 000 nm. Conoscopic image was used to study the homogeneity of the crystals which was observed using 532-nm laser as a light source. Ultramicroscopy which has been widely used in detecting defects of crystals was used to investigate the scattering centers in the crystals using the laser of 532 nm[13].

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:YLF laser were focused by a lens with $f = 500$ mm into the material. The pulse width of 1 053 nm, 526 nm (full-width of half-maximum, Gaussian shapes) is 18 ns, 15 ns respectively. The laser ran at a repetition rate of 1 Hz. For 1ω and 2ω waves, the spot areas of the laser beam were 0.18 mm^2, 0.25 mm^2 respectively.

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 (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 Fe^{3+}, Cr^{3+}, Al^{3+}) tends to exist in the prism sector of the crystal[14]. 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 ultraviolent 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 400–1 800 nm 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.

Figure 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.

Conoscopic image is used to study the optical homogeneity of the crystals. Figure 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

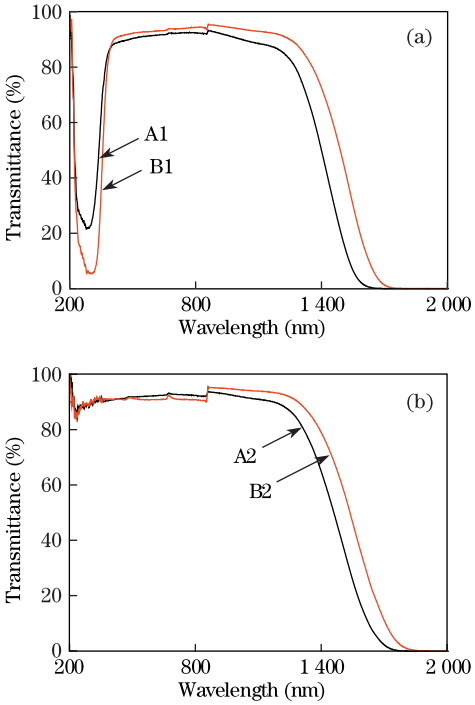


Fig. 3. Transmission spectra of the KDP and DKDP crystals. (a) Samples A1 and B1; (b) samples A2 and B2.

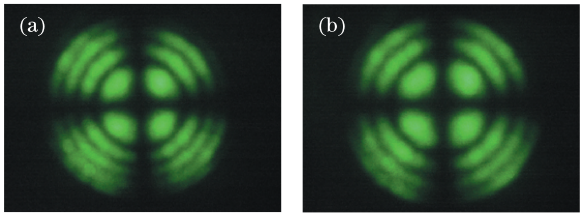


Fig. 4. Conoscopic figures of [001] crystal plate sample. (a) Sample A1; (b) sample B1.

the effect of the D element on the microstructure of the crystal, rocking curves and lattice constant were measured.

Figure 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.

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.

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 B.

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 1 053 nm is 2.5-3.8× that for damage testing at 526 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 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.

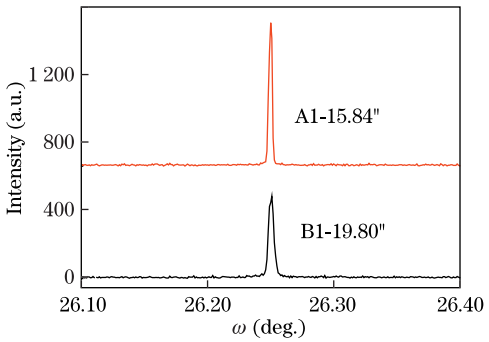


Fig. 5. Rocking curves of HRXRD on sample A1 and sample B1.

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

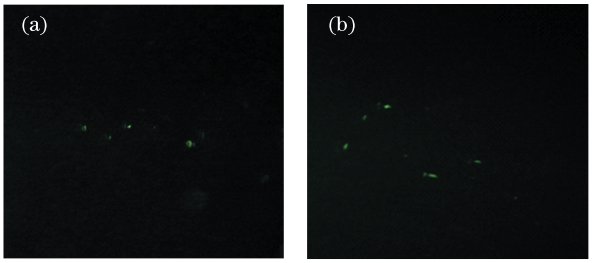


Fig. 6. Morphology of scattering centers in samples A1 and B1. (a) Sample A1; (b) sample B1.

Table 2. LDT of Crystal Samples

No.	LDT /(J/cm^2, 1 053 nm, 18 ns)	LDT /(J/cm^2, 526 nm, 15 ns)
A1	33.54	9.23
A2	20.21	5.95
B1	23.26	9.16
B2	18.49	4.85

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 infrared absorption edge of the transmission spectra is obviously red-shifted but the crystalline perfection and optical homogeneity of DKDP crystal become poorer. 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 1 053 nm has a 2.5-3.8× increase compared with that tested at 526 nm and LDT of Z-cut samples is obviously higher than that of the type-II tripling-cut samples whether for 1ω or for 2ω.

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