Effect of raw material and growth method on optical properties of DKDP crystal

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Three kinds of KH_2PO_4 raw material are used to grow deuterated potassium dihydrogen phosphate (DKDP) crystals by traditional and rapid growth methods, respectively. The growth habit dependence on the purity of raw material is described and analyzed. The optical properties including transmission spectra and laser-induced damage threshold of these crystals are measured. It is found that the growth method affects the optical properties of crystal more obviously than the raw material with the mass content of main metal ions below 1 ppm. Moreover, the morphology of the core in the observed damage sites indicates that an explosion process probably occurs during laser-induced breakdown.

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Potassium dihydrogen phosphate (KDP) crystals are the materials of choice for frequency conversion and electro-optical switching incorporated in the high-power laser systems under development aiming to achieve fusion in the laboratory[1–3]. The partially deuterated KDP (DKDP) crystal was used as tripler frequency converter to minimize an otherwise strong transverse stimulated Raman scattering[4,5]. However, a key factor limiting the energy produced by the high-power lasers is the weak resistance of the crystal to laser damage. It is therefore necessary to improve laser damage resistance through optimizing crystal growth conditions.

Laser-induced damage is observed in the bulk of the best current KDP material at laser fluences estimated to be more than one order of magnitude below the intrinsic breakdown threshold of pure material[6]. The process has been attributed to pre-existing damage precursors incorporated or formed during growth process. The laser-induced damage threshold (LIDT) of DKDP crystal dependent on the growth conditions shows that laser damage is caused by extrinsic nanoparticles or intrinsic defects[7,8]. And recently the electronic structure of these defects can be determined approximately[9,10]. Nevertheless, the optical growth conditions by which these precursors can be eliminated in KDP/DKDP crystals are unknown.

In this letter, three kinds of raw material with relative high purity are used to grow DKDP crystal by traditional and rapid methods, respectively. The optical properties of these crystals are measured. The effect of raw material and growth method on these properties was analyzed. Here it has been found that the growth method affects the crystal's optical properties more obviously than the raw material with the mass content of main metal ions below 1 ppm.

DKDP crystals were grown from deuterated aqueous solution made by high purity heavy water (99.9%, D_2O), de-ionized H_2O, and KH_2PO_4 raw material. The deuterated degree of growth solution is around 87%, which can get DKDP crystals with a mole% D content of 82%[11]. Three kinds of KH_2PO_4 raw material (named as A, B, and C, respectively) are used in the experiment. The content in mass of the main metallic ionic impurity in the KDP material used for synthesis is shown in Table 1. The growth solutions were filtered through a 0.22 μm membrane and then overheated at 70 °C for 24 h in crystallizer that was placed in a water bath of temperature fluctuation less than ±0.02 °C. The plate seed crystals (50×50×7 (mm) in dimension) and "point seed" (5×5×5 (mm) in dimension) were used in the traditional cooling method and rapid growth method, respectively. Crystallization was performed in a temperature range of 52–32 °C. For traditional growth, the

Table 1. Mass Content of Main Metallic Ionic Impurity in Raw Materials[a]

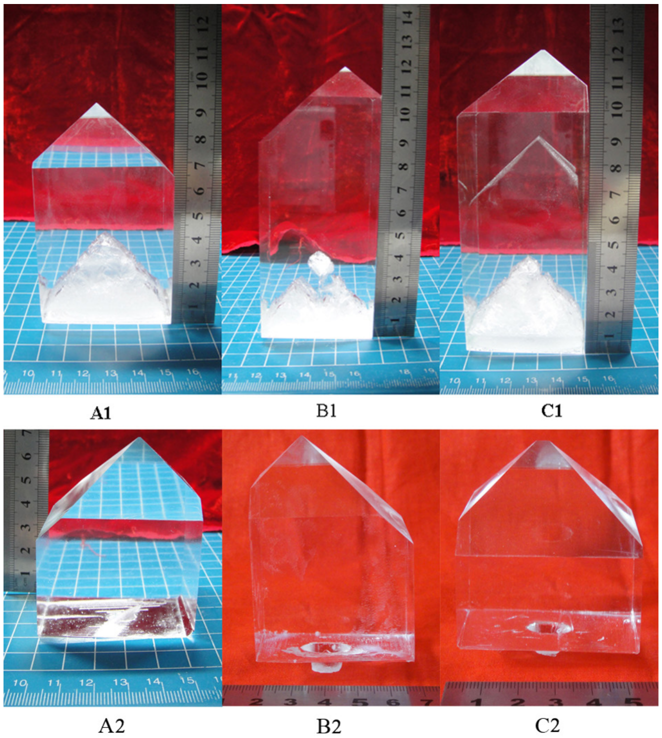
Element (ppm)	Fe	Co	Mn	Mg	Cu
A	0.1	0.01	0.01	0.5	0.005
B	0.105	0.033	0.059	0.021	0.018
C	1	0.1	0.1	0.1	0.1

[a]Amounts are in nanograms per gram KDP.

Table 2. Growth Parameters of DKDP Crystals Grown with Different Raw Materials by Traditional Cooling Method and Point-seed Technique, respectively

No.	**Raw Material**	**Seed Type**	**Crystal size (mm) (a×b×c)**	**Temperature Reduction Range (°C)**	**Rotation Speed (r/min)**	**Growth Rate (mm/d)**	
						a-direction	**c-direction**
A1	A	Z-plate	53×53×91	50–34.1	30	/	0.6
B1	B	Z-plate	51×51×124	52.5–34.9	30	/	0.8
C1	C	Z-plate	51×52×125	51–34.1	30	/	0.9
A2	A	Point	48×55×67	48–35.2	77	2.3	5.6
B2	B	Point	43×48×66	50.3–39.4	77	1.5	4.2
C2	C	Point	47×50×53	48.5–38.3	77	1.6	3.3

plate seed grew at a temperature about 0.5 °C below the saturation temperature and rotated with a speed of 30 rpm. For point-seed rapid growth, the solution temperature was lowered to at a temperature about 3 °C below the saturation temperature instantly and the point seed began to rotate at a speed of 77 rpm. The information of the as-grown DKDP crystals is given in Table 2. There are no visible macroscopic defects in these crystals. A typical picture of these crystals visualized along [010] direction is shown in Fig. 1.


A1 B1 C1

A2 B2 C2

Fig. 1. Photograph of the as-grown DKDP crystals along the [010] direction. Samples A are grown from the purest raw material A, samples B are grown from the less pure raw material B, and samples C are grown from the least pure raw material C. 1 – the crystals are made by conventional growth and 2 – by rapid growth.

DKDP crystals were, respectively, cut in two commonly used orientations: optical axis parallel to the z-axis, otherwise known as z cut and type II frequency conversion orientation with the optical axis tipped at 59° from the z-axis, otherwise known as tripler cut. Then the surfaces were oriented by X-ray diffraction with accuracy in $\pm 7''$, and fine polished. The sample thickness was about 10 mm. The same growth condition of the DKDP crystals and the fine processing for the sample can ensure the reproducibility of the damage results.

The transmittance spectra of the z cut samples in the region of 200–1900 nm were measured by means of Hitachi U-3500 spectrometer. The bulk LIDT was measured using an injection-seeded laser of Q-switched Nd:YAG laser (0.355 μm) operating in transverse and single longitudinal modes, and the experimental schematic is shown in Fig. 2. The laser was operated at the repetition rate of 1 Hz with the pulse width of 8 ns. The pulse laser had a Gaussian spatial profile. To avoid surface damage of crystals, the laser beam of 0.66 μm diameter was focused on the rear face of DKDP crystal by a lens with a focal length of 5000 mm. The

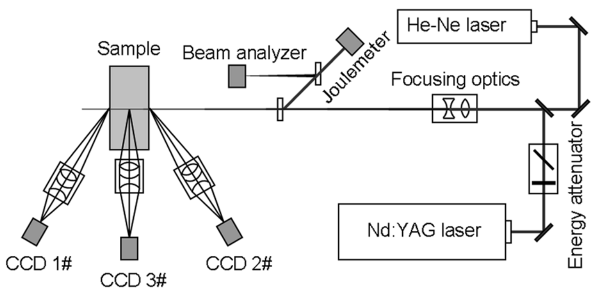


Fig. 2. Experimental bench for the measurement of bulk LIDT in DKDP crystals.

occurrence of damage was determined by the observation of a white plasma spark in CCD monitor, and a scattered He–Ne laser was used to confirm a small damage spot. The LIDTs were measured using two procedures[12]: 1/1 tests and R/1 tests. For 1/1 procedure 15 sites were irradiated to get the damage probability for a given fluence, linear extrapolation of the damage probability data to zero damage probability yields the threshold energy, whereas 50 test sites were used in the R/1 procedure. The starting fluence is about 1 J/cm^2 and the fluence step is about 1 J/cm^2. The LIDT for R/1 test is the maximum fluence without damage occurring. The total systematical error of the fluence is about 12%.

Figure 1 shows the morphology of the DKDP crystals grown by conventional temperature reduction method and point seed technique, respectively. It can be seen that there are no visible macroscopic defects in these crystals except crystal C1 which was grown by conventional method with the least pure raw material C. The inclusions in crystal C1 formed as a result of temperature fluctuation. Moreover, the crystal C1 is obviously tapering during the growth process. This phenomenon disappears finally and the recovered region on tapered face has a bit of a green color. It is well known that the presence of trivalent metal ions, such as Fe^{3+}, Al^{3+}, Cr^{3+}, affect the growth rate, morphology, and quality of KDP-type crystals grown from aqueous solutions, and that the effect of impurities is particularly marked for the growth of the prismatic faces of the crystals[13]. The impurities of high concentration in the solution retarded growth of (100), which is the main cause for tapering. The solution made with raw material B has higher stability compared with those made with A and C. Extraneous crystals were not formed there when some floccules arise in the growth solution at lower temperature.

The transmission spectra with wavelength ranging from 200 to 2000 nm of these DKDP crystals are shown in Fig. 3. It is clear that these crystals have sufficient transmission in the entire visible and IR region. A comparison between these transmission spectra shows that they are similar above λ =400 nm or so, whereas strong differences appear for λ ≤ 400 nm. The crystals grown by traditional method have higher transmission efficiency in UV region than those crystals grown by rapid method. As for rapidly grown crystals, the prismatic sector had stronger absorption than the pyramidal sector particularly in UV region as reported by other research (see Fig. 2 in Ref. [14] and Fig. 1 in Ref. [15]). It is generally known that the metal ions can easily incorporate into the prismatic sector of KDP crystal and then cause the absorption[14]. Moreover, for rapidly grown crystals the data clearly indicate the presence of an intense 270 nm optical absorption band. These absorption bands can be attributed to the presence of Fe in the crystal bulk as previously reported[15]. Another interesting feature, common to all the tested crystals, is the discrepancy between transmission of the conventional grown crystals and the ones grown by rapid method in the range from 800 to 1900 nm. Due to slight differences in the D concentration on different faces of the growth hillock[1,7], the deuteration level of the traditional grown crystal may be a little higher than that of the rapid grown crystal. The shift toward longer wavelength of the transmission edge in the case of traditional grown crystal arises from the weak bond strength of D–O compared with H–O[16].

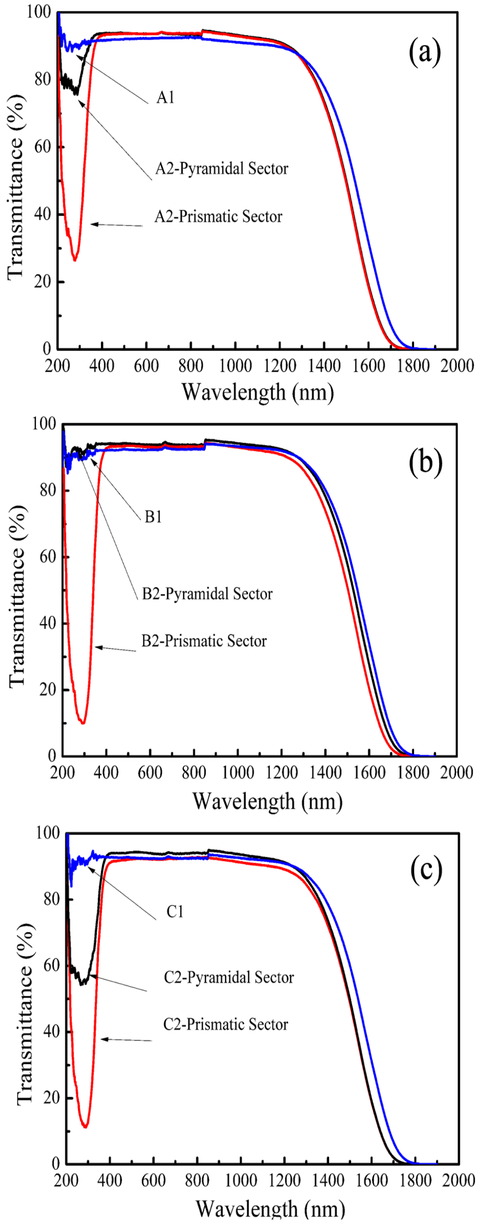


Fig. 3. Transmission spectra of DKDP crystals grown with raw materials (a) A, (b) B, and (c) C. Blue dots – crystal grown by traditional method, black dots – pyramidal sector of crystal grown by rapid method, and red dots – prismatic sector of crystal grown by rapid method.

Table 3. LIDTs of DKDP Crystal Samples

Tripler	**0%LIDT (J/cm^2)**			**(355 nm, 8 ns)**		
	Traditional			**Rapid**		
	1/1	**R/1**	**Gain**	**1/1**	**R/1**	**Gain**
A	8.5	16.9	2.0X	8.5	13.9	1.6X
B	9.6	13.9	1.4X	7.2	11.1	1.5X
C	8.1	15.8	2.0X	8.8	12.8	1.5X

The LIDTs of the tripler samples cut from these crystal are listed in Table 3. The samples were measured by 1/1 and R/1 damage testing, respectively. From these data, the results can be summarized as follows: 1) except the 1/1 testing result of the crystal C, the LIDT of the crystals grown by traditional method is commonly higher than that of the crystal grown by rapid technique. The lower LIDT for rapidly grown crystals can be considered to arise from the formation of intrinsic defects or the incorporation of metal ions under high supersaturation. 2) Compared with the 1/1 testing, the R/1 testing can obviously enhance the damage resistance of the sample. The 1/1 test program uses one laser shot on each unexposed site in the sample, R/1 testing is a way of testing dozens of shots on each site with the fluence ramping up until damage occurs. The exposure at sub-damage fluences can improve the laser-induced damage resistance of a crystal[17]. The mean gain of the enhancement for crystal grown by traditional method is higher than that of crystal grown by rapid method. 3) With identical starting growth temperature and temperature reduction interval, damage resistance in DKDP is fairly independent of raw material with the mass content of main metallic ionic impurity below 1 ppm, as it can be seen from that the deviation of LIDT for these crystals is slight. Considering the smaller size of crystal and less fluctuation of the temperature reduction rate during growth process, this conclusion confirms the results previously reported[18].

The 1/1 testing damage probabilities curves of these DKDP crystals are shown in Fig. 4. For conventional growth, the difference in raw materials does not lead to visible variation of damage probabilities between the three crystals A1, B1, and C1. From Figs. 4(a) and (b), it can be seen that the rapid grown crystals resist to damage poorly compared with the conventional grown crystal. However, the crystal of rapid growth with lower growth rate (e.g., about 3 mm/d for crystal C2) could have more excellent damage resistance than the one of conventional growth. The damage sites are observed by using microscope. We find that the damage sites irradiated by 355 nm laser consist of three distinct regions which are shown in Fig. 5, which are in agreement with previous reports[19,20]. The diameter of the core is ranging from 2 to 30 μm, mainly distributing in the region below 10 μm. The morphology of the cracks are star-like, with four-fold symmetry which is similar to the highest order symmetry axis in structure of DKDP crystal[21]. From Fig. 6, it can be seen that the core is partially filled with rubble. It indicates that there may exist an explosion process during laser-induced breakdown.

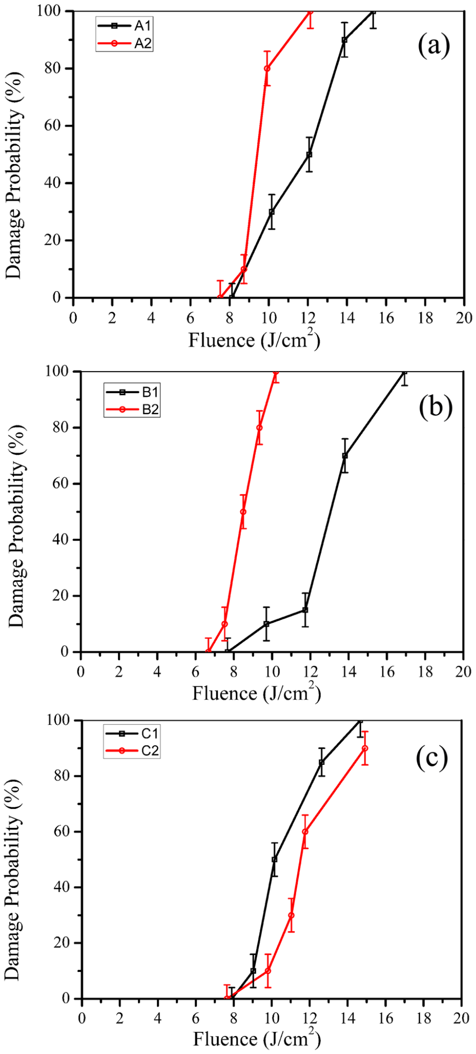


Fig. 4. Bulk damage probability curves of DKDP crystal for 355 nm using tripler samples. (a) A1, A2, grown with raw material A, (b) B1, B2, grown with raw material B, and (c) C1, C2, grown with raw material C.

In conclusion, three kinds of KH_2PO_4 raw materials with high purity are used to grow DKDP crystals by traditional and rapid methods, respectively. As for the rapid growth, the solution prepared using raw material with high purity is more favorable for crystallization. Growth method plays the dominant role in affecting the transmission property of the crystals in the UV region. Maybe due to slight differences in the deuterium concentration on different faces of the growth hillock, the

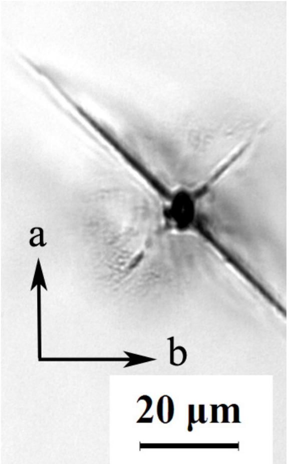


Fig. 5. Bulk damage site in DKDP crystal initiated with 355 nm laser, detected by optical microscopy along the direction perpendicular to laser beam.

transmission edge of traditional grown crystal shifts toward longer wavelength in the IR region compared with that of rapidly grown crystal. With identical starting growth temperature and temperature reduction interval, the damage resistance in DKDP is fairly independent of raw material with the mass content of main metallic ionic impurity below 1 ppm.

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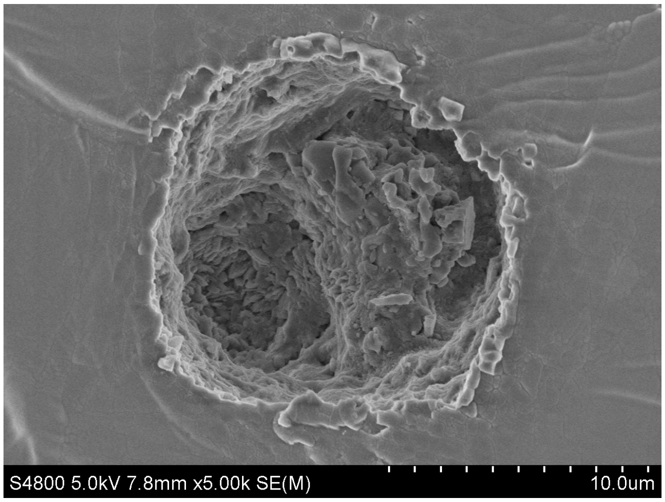

Fig. 6. Graph of the core partially filled with rubble observed by SEM.

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