crystals

MDPI

Article

Research on Nonlinear Absorption Effect in KDP and 70%-DKDP Crystals

Duanliang Wang [1,2,3], Shenglai Wang [1,3,*], Jiyang Wang [1], Chuanying Shen [2], Weidong Li [1,3], Pingping Huang [1,3], Hui Liu [1,3] and Robert I. Boughton [4]

1 State Key Laboratory of Crystal Materials and Institute of Crystal Materials, Shandong University, Jinan 250100, China; wdliang012@163.com (D.W.); jywang@sdu.edu.cn (J.W.); li2wei3dong@163.com (W.L.); liunian_nuanyang@126.com (P.H.); liuhui19901219@126.com (H.L.)
2 Shandong Provincial Key Laboratory of Laser Polarization and Information Technology, College of Physics and Engineering, Qufu Normal University, Qufu 273165, China; shenshouchuan@163.com
3 Key Laboratory of Functional Crystal Materials and Device, Shandong University, Ministry of Education, Jinan 250100, China
4 Department of Physics and Astronomy, Bowling Green State University, Bowling Green, OH 43403, USA; boughton@bgsu.edu
* Correspondence: slwang67@sdu.edu.cn

Academic Editor: Shujun Zhang
Received: 7 May 2017; Accepted: 17 June 2017; Published: 1 July 2017

Abstract: Nonlinear optical absorption effect in KDP and 70%-DKDP crystals, which were grown by the conventional temperature cooling method, was systematically studied using picosecond pulse laser excitation. Using open aperture Z-scan measurements, the dependence of nonlinear absorption effect on sample orientations (I, II, and z) as well as laser intensity was systematically measured at λ = 1064 and 532 nm. According to the experimental results, the nonlinear absorption effect at λ = 532 nm was confirmed, while at λ = 1064 nm no nonlinear absorption was observed for KDP and 70%-DKDP crystals. In addition, the optical absorption along I- and II-type affected by laser intensity was larger than that along the z-direction. The important nonlinear absorption coefficients β and $\chi_I^{(3)}$ (esu) measured along different orientations were exhibited in detail at wavelengths of 1064 nm and 532 nm. The results indicate that nonlinear absorption coefficients increase first and then decrease with the increment of laser intensity for KDP and 70%-DKDP crystals.

Keywords: nonlinear absorption effect; Z-scan; KDP and 70%-DKDP crystals

1. Introduction

KH_2PO_4 (KDP) and $KD_{2-x}H_xPO_4$ (DKDP) crystals, a kind of nonlinear optical material, find wide application as optical-electric conversion devices and multiple frequency converters [1–4]. They have wide applications in high-power laser systems, especially the Inertial Confinement Fusion system (ICF) [5,6]. However, laser-induced damage, which results from the interaction of laser pulses with KDP or DKDP crystals, may be produced, which then decreases laser conversion efficiency. This has become a main drawback in limiting the applications of KDP and DKDP crystals [7,8]. As is well known, laser-induced damage usually initiates the absorption of laser energy. In the process, self-focusing, self-phase, or cross-phase modulation (XPM) and nonlinear optical absorption effects may be induced [9–11]. In particular, nonlinear optical absorption is a main factor in decreasing the efficiency of harmonic generation, and can even lead to photoionization and electron avalanche breakdown. However, nonlinear optical absorption that has been correlated with laser intensity, laser wavelength, or crystal orientation has not yet been characterized in detail. Clearly, a better understanding of nonlinear optical absorption properties is essential.

Based on spatial distortion and the relationship between transmitted light and energy transfer up-conversion, the Z-scan method is an effective way to determine nonlinear absorption behaviors (both saturable and reverse saturated absorption) [12–15]. Moreover, the nonlinear absorption coefficient (β), one of the most important nonlinear optical parameters, can be calculated from the measured results. In this work, taking advantage of the Z-scan method, nonlinear absorption characteristics of KDP and DKDP (with 70% deuterium) crystals were measured under picosecond laser pulse irradiation. The corresponding nonlinear absorption coefficient β along different crystal orientations were also determined. Furthermore, the dependence of nonlinear absorption effect on laser wavelength (λ = 1064 and 532 nm), irradiation intensity, and crystal orientation is discussed.

2. Experimental

KDP and DKDP (with 70% deuterium) crystals were grown using the conventional growth method with a z-axis seed, as shown in Figure 1. On the basis of the schematic diagram plotted in Figure 2a, samples of z-cut, I- and II-type were obtained from the as-grown crystals. All samples were cut to the dimensions of 10 mm × 10 mm × 1.5 (thickness) mm and underwent double-sided polishing, as shown in the inset of Figure 2a.

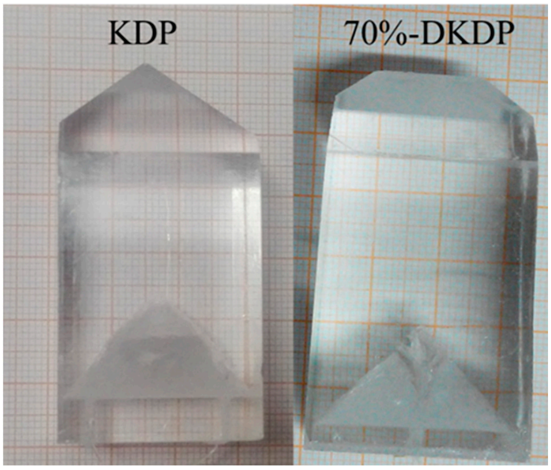

Figure 1. Photographs of the as-grown KDP and 70%-DKDP crystals.

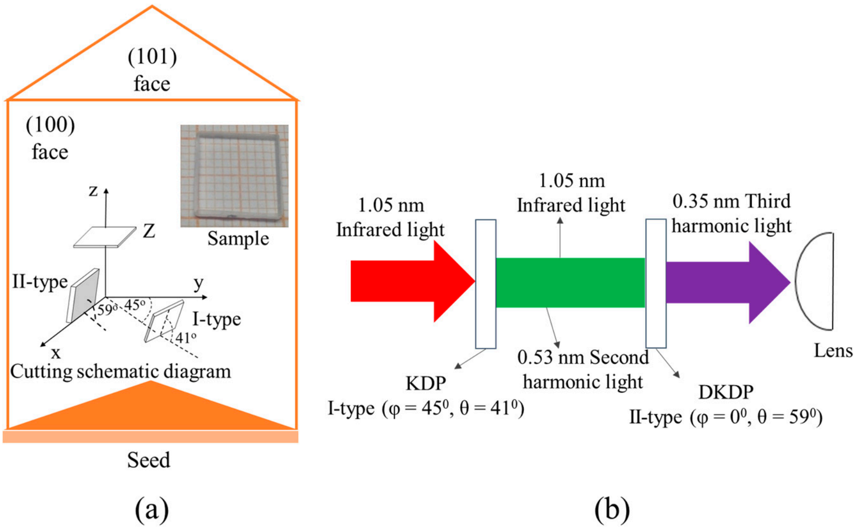

Figure 2. (**a**) Cutting schematic diagram of samples with different directions; (**b**) The mechanism diagram for KDP/DKDP crystals in Inertial Confinement Nuclear Fusion (ICF).

As shown in Figure 2b [5,6], large-scale KDP and DKDP crystals are placed in ICF systems, particularly II-type and I-type oriented samples, to be used as frequency conversion devices. In the present experiment, nonlinear absorption properties were explored by the Z-scan technique. The schematic diagram of an open-aperture Z-scan is depicted in Figure 3 [12]. During the measurement, the sample was transferred from +z to −z, and then the data was collected by Detector 1 and Detector 2, which represent the reference light and measuring optical path, respectively.

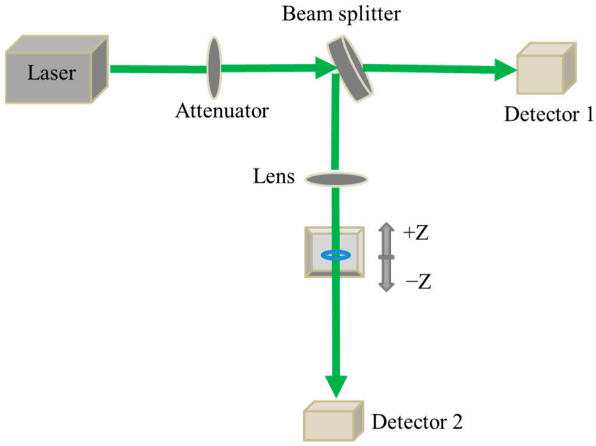

Figure 3. Schematic diagram of an open-aperture Z-scan.

In principle, the dependence of laser intensity on sample position can be monitored by a computer in real time. Through data analysis, the nonlinear absorption information for KDP and DKDP crystals can be easily acquired. A mode-locked Nd:YAG laser with a wavelength of 1064 nm was used as the laser source (pulse duration of 40 ps and repetition rate of 10 Hz). The frequency doubled laser emission at λ = 532 nm, with a pulse width of 30 ps was generated by a high-quality KTP crystal, with a lens focal length of about 30 cm. Using open-aperture Z-scan measurements [16,17], the nonlinear absorption characteristics at λ = 1064 nm and 532 nm were investigated in detail. For each sample, several experiments were carried out by changing the sample location to ensure the existence and accuracy of the nonlinear absorption effect.

3. Results

3.1. Nonlinear Absorption Characteristics of KDP and 70%-DKDP Crystals at λ = 1064 nm

Figure 4 shows the normalized transmittance curves of KDP and 70%-DKDP obtained by an open-aperture Z-scan. The results with different laser power intensities were derived from measurements on the II-type, and revealed the features in common with z-cut and I-type samples at λ = 1064 nm. The dashed line represents the experimental data and the red solid line is the fitted results using Equations (1) and (2) [18,19]:

$$T = \sum_{m=0}^{\infty} \frac{\left[\frac{-\beta I_0 L_{eff}}{(1+z^2/z_0^2)}\right]^m}{(m+1)^{3/2}} \tag{1}$$

$$L_{eff} = [1 - \exp(-\alpha_0 L)]/\alpha_0 \tag{2}$$

where L_{eff}, L, I_0 and α_0 are the effective thickness, thickness, peak intensity, and linear absorption coefficient, respectively. $z_0 = \pi\omega_0{}^2/\lambda$ is the diffraction length of the focused beam, λ is the wavelength of the beam and z is the sample position. From the results in Figure 4, it is clear that theoretical results agree well with the experimental data for KDP and 70%-DKDP crystals. The horizontal line of the Z-scan results indicates no obvious nonlinear response under the given conditions. Moreover, the measurements with different intensities below I_0 = 94 GW/cm^2 yield similar conclusions. In other words, for I_0 less than 94 GW/cm^2, no obvious nonlinear absorption effect is detected in KDP and 70%-DKDP crystals at λ = 1064 nm.

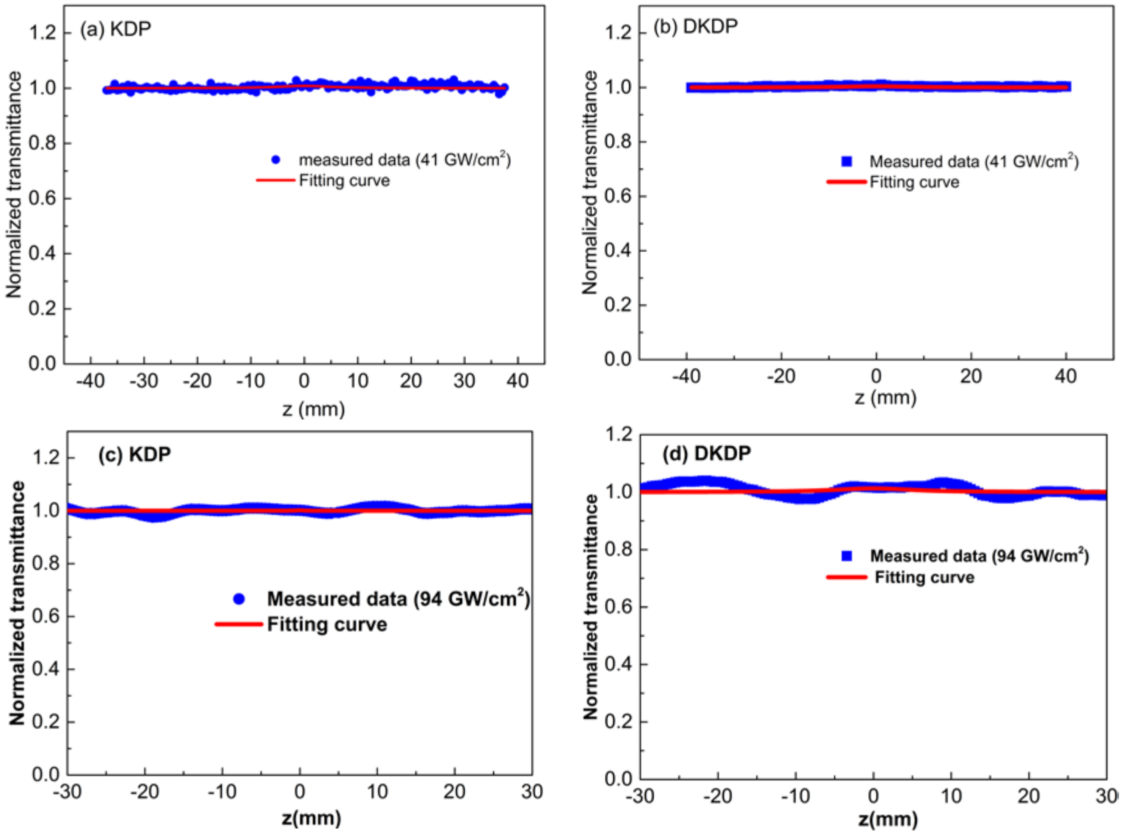

Figure 4. At λ = 1064 nm, open aperture Z-scan data and fitted curves of II-type for KDP and 70%-DKDP crystals under different laser intensities: (**a**) KDP under 41 GW/cm^2, (**b**) DKDP under 41 GW/cm^2, (**c**) KDP under 94 GW/cm^2, (**d**) DKDP under 94 GW/cm^2.

3.2. Nonlinear Absorption Characteristics of KDP Crystal at λ = 532 nm

At 532 nm, the normalized transmittance curves under the open aperture Z-scan are displayed for KDP crystal in Figure 5. From the figure, an obvious characteristic resembling a sharp valley at the focal point is evident, indicating the existence of a nonlinear absorption response. More importantly, a dependence of nonlinear absorption characteristics on orientation and laser intensities is displayed. Apparently, nonlinear absorption produced by picosecond laser irradiation exhibits a significant difference with different orientation. Compared to the I- and II-type orientations, nonlinear absorption along the z-direction occurs at a lower laser intensity. To a certain degree, this phenomenon verifies the anisotropic nature of nonlinear absorption, and reflects the intrinsic properties of KDP crystal. For each sample along the z-cut, I- or II-type, an additional feature is that the amplitude of the valley at the focus point becomes larger with the enhancement of the laser intensity.

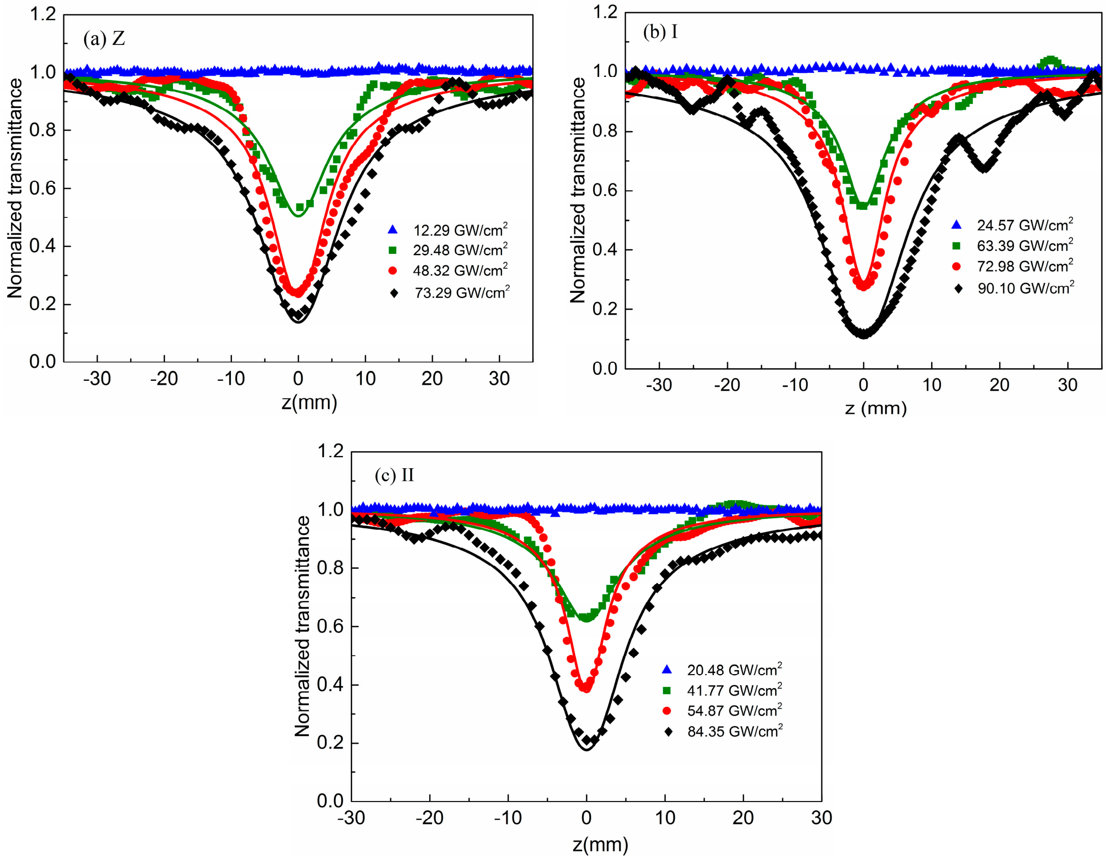

Figure 5. Open aperture Z-scan data and fitted curves for KDP samples with different intensities at λ = 532 nm: (**a**) z-direction, (**b**) I-type, (**c**) II-type.

The dotted and solid lines in Figure 5 respectively represent the measured data and the fitted results given by Equation (1). The fitted results are quite consistent with the experimental data. From the fitted results and Equation (2), the corresponding nonlinear absorption coefficients β are calculated and summarized in Table 1. The imaginary part $\chi_I^{(3)}$ of the third-order susceptibility, which is correlated with the nonlinear absorption coefficient β, is calculated using the following formulas [16,18,20]:

$$\Delta\varphi_0 = \beta I_0 L_{eff}/2 \quad (3)$$

$$\chi_I^{(3)}(esu) = c^2 n_0^2 \beta / 240\pi^2 \omega \ (m/W) \quad (4)$$

where n_0 is the linear index of refraction and ω is the optical frequency. Thus, the corresponding results on $\chi_I^{(3)}$ (esu) in different orientations are shown in Table 1. Based on the measured graphical and calculated values, the relationship between the nonlinear absorption effect and the orientation and intensity was acquired in detail for KDP crystal. In contrast to I- and II-type, the nonlinear absorption coefficient β along the z-cut is determined to be in the range from 1.75×10^{-10} cm/W to 3.30×10^{-10} cm/W, while the corresponding values along I- and II-type range from 1.46×10^{-10} cm/W to 1.61×10^{-10} cm/W and 1.49×10^{-13} esu to 2.01×10^{-13} esu, respectively. For the z-direction, an obviously characteristic is shown; as the laser intensities increase, the nonlinear absorption coefficient β decreases with the increasing absorption degree. For I-type and II-type, the values of β increase during the process of enhancing the laser irritation to a certain extent, but then the absorption coefficients decrease as the laser intensity increases further. This implies that a close dependency is displayed between the absorption coefficient and light intensity. In addition, the values along I- and II-type change significantly under the higher laser power intensity, compared to previous studies [21].

This means that nonlinear absorption, including the two-photon and even multi-photon effect, may be induced initially. From the results analysis, the value along the z-direction is greater than that along I- and II-type, and the I-type has a somewhat smaller value than II-type. Consequently, a KDP sample along the z-cut is apt to generate nonlinear absorption under the same conditions. Damage caused by nonlinear absorption is more likely to occur for the z-direction. From this perspective, it is also demonstrated that I-type or II-type KDP samples are more suitable for applications in high-power systems as frequency conversion devices [22].

Table 1. Calculated results of nonlinear absorption parameters for KDP crystals at λ = 532 nm.

Crystal and Laser Power Density (GW/cm^2)	**KDP**								
	Z			**I**			**II**		
	29.48	**48.32**	**73.29**	**63.39**	**72.98**	**90.10**	**41.77**	**54.87**	**84.35**
β (10^{-10} cm/W)	3.30	2.53	1.75	1.46	1.61	1.47	1.98	2.01	1.49
$\chi_I^{(3)}$ (10^{-13} esu)	4.95	3.79	2.63	2.19	2.41	2.20	2.97	3.01	2.24

3.3. Nonlinear Absorption Characteristics of 70%-DKDP Crystal at λ = 532 nm

The open aperture Z-scan results on 70%-DKDP at different intensities and orientations are perspicuously illustrated in Figure 6, which closely resembles the KDP results. Under lower intensity laser irradiation, the horizontal lines reveal that there is no nonlinear absorption at 532 nm. At the appropriate radiation intensity for different samples, nonlinear absorption can be produced and a valley-like dip appears in the normalized transmittance. According to the results, the laser intensity necessary to produce the nonlinear absorption effect along the z-direction is significantly smaller than that required for the I- and II-type, but there is no obvious rule correlation displayed between them. Any such correlation is mainly due to the essence of crystal anisotropy.

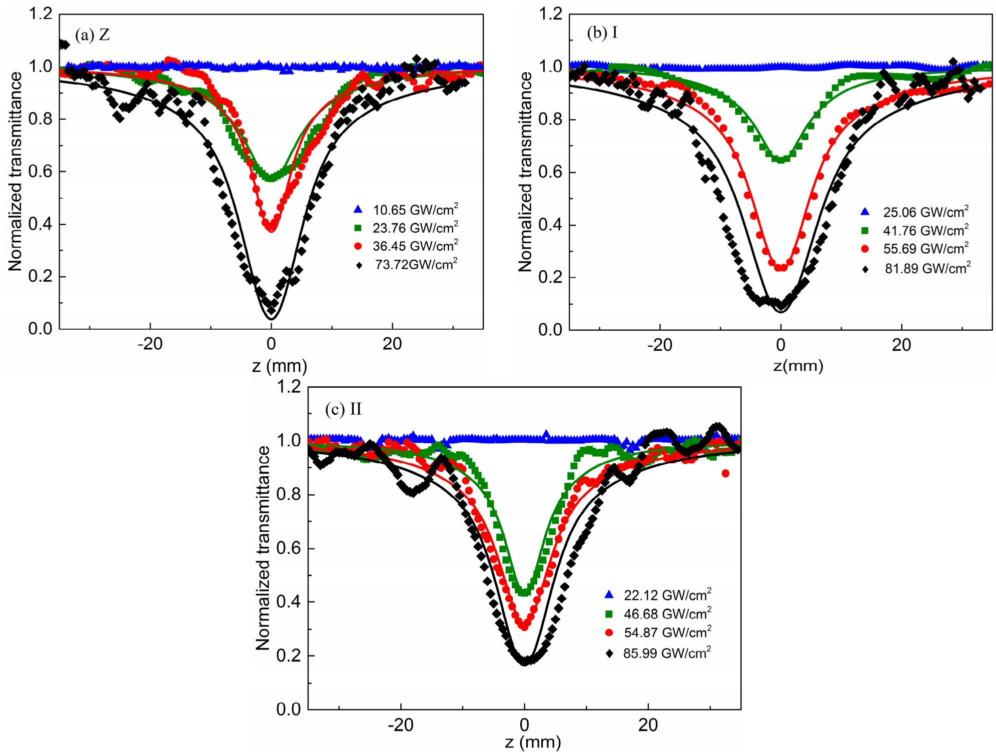

Figure 6. Open aperture Z-scan data and fitted curves for 70%-DKDP samples with different intensities at λ = 532 nm: (**a**) z-direction, (**b**) I-type, (**c**) II-type.

Upon analyzing Figures 5 and 6, the generation of nonlinear absorption for 70%-DKDP seems to be easier than KDP crystal. Similarly, the corresponding values of $\Delta\varphi_0$ are obtained from the fitted results by using Equation (1). Through Equations (3) and (4), nonlinear parameters including β and $\chi_I^{(3)}$ (esu) were calculated, and are listed in Table 2. It is clear to see that the values of β along the I, II and z-direction vary from 1.62×10^{-10} cm/W to 2.20×10^{-10} cm/W, 1.47×10^{-10} cm/W to 2.25×10^{-10} cm/W, and 1.83×10^{-10} cm/W to 3.80×10^{-10} cm/W, respectively. Similar to KDP crystal, the parameters including β and $\chi_I^{(3)}$ (esu) of 70%-DKDP exhibit significant differences at different orientations due to the anisotropic nature of the crystal. The nonlinear absorption coefficient along the z-direction is larger than that along I- and II-type, while the value along the I-type displays a comparatively smaller value among the samples. Also, the nonlinear absorption coefficient along I- and II-type increases first and then decreases with the increment of laser intensity [21]. In addition, nonlinear absorption for 70%-DKDP seems to be somewhat greater than the same category in KDP crystal.

Table 2. Calculated results of nonlinear absorption parameters for 70%-DKDP crystal at λ = 532 nm.

Crystal and Laser Power Density (GW/cm^2)	70%-DKDP								
	Z			I			II		
	23.76	36.45	73.72	41.76	55.69	81.89	46.68	54.87	85.99
β (10^{-10} cm/W)	3.80	3.03	1.83	1.92	2.20	1.62	2.25	2.10	1.47
$\chi_I^{(3)}$ (10^{-13} esu)	5.69	4.55	2.74	2.87	3.29	2.43	3.37	3.14	2.20

3.4. Discussion

From the above results, one of the remarkable features is that the nonlinear absorption effects in KDP and 70%-DKDP crystals are clearly exhibited at λ = 532 nm, whereas there is no nonlinear absorption at λ = 1064 nm for a laser intensity less than 94 GW/cm^2. This result reveals that the nonlinear absorption effects in KDP and 70%-DKDP crystals are correlated with the laser wavelength. For nonlinear optical crystals, the existence of nonlinear absorption may substantially decrease the frequency conversion efficiency, and even lead to internal damage at 532 nm [22].

Another determination is that nonlinear absorption in these crystals is affected by crystal orientations, indicating that crystal structure plays a decisive role in the nonlinear absorption effect, especially the configuration of $H_2PO_4^-$ and $D_2PO_4^-$ groups. In addition, I- and II-type with lower nonlinear absorption effects are more specifically suited to applications as frequency conversion devices, with higher frequency conversion efficiency and less crystal damage [22]. It is proposed that the crystal structure is responsible for the variation of the nonlinear absorption effect, including the nonlinear optical parameters β and $\chi_I^{(3)}$ (esu).

In addition, laser intensity may be a crucial factor affecting nonlinear absorption in KDP and 70%-DKDP crystals, especially at 532 nm. No nonlinear absorption effect in samples of I- and II-type was observed in the laser intensity range from about 20.48 to 25.06 GW/cm^2, and in the z-directions over the range from about 10.65 to 12.29 GW/cm^2. However, all of the samples produce a marked nonlinear absorption effect when laser intensity reached a particular threshold intensity along the respective direction. This indicates that the generation of nonlinear absorption is closely related to the laser intensity. In particularly, nonlinear absorption in all the samples significantly increased with an increase in laser intensity. This phenomenon also indicates that crystal damage originating from nonlinear absorption, which can decrease the utilization efficiency of these crystals as optical components, may be enhanced as the laser intensity increases. In addition, the results imply that nonlinear absorption coefficients decrease when the laser intensity exceeds a critical value. Because of the complexity of nonlinear effects in high-power laser systems, this may be associated with the crystalline essence.

The calculated results illustrate that there exist certain differences in the nonlinear absorption coefficients between KDP and 70%-DKDP crystals. In comparison to KDP crystal, the nonlinear absorption coefficients of 70%-DKDP show a slight tendency to be greater. This variation may be associated with the generation of D–O bonds. In the process of DKDP growth, H–O bonds are gradually replaced by D–O bonds with a relatively weaker bonding force [21,23–25]. Through the above analysis, $H_2PO_4^-$ and $(D_xH_{1-x})_2PO_4^-$ groups play a crucial role in nonlinear absorption for KDP and 70%-DKDP. More importantly, the resulting parameters of β and $\chi_I^{(3)}$ (esu) have extremely favorable values. In contrast to previous results, such as dye-doped KDP (β = 141 cm/GW), KDP at λ = 216 nm ($\beta = 6.0 \pm 0.5 \times 10^{-10}$ cm/W), and L-lysine doped $NH_4H_2PO_4$ (ADP) ($\beta = 4.063 \times 10^{-6}$ cm/W) [16,26,27], a lower nonlinear absorption coefficient is displayed for pure KDP and 70%-DKDP crystals, especially I- and II-type. This means that I- and II-type crystals with a higher utilization efficiency can be applied as frequency conversion devices, while those with the z-direction with no nonlinear absorption at λ = 1064 nm and larger values at λ = 532 nm are more suited to be employed as optical switch devices. In summary, it is clear that all these results provide significant guidance to the applications of KDP and 70%-DKDP crystals, particularly in high-power laser systems.

4. Conclusions

To sum up, the nonlinear absorption characteristics of KDP and 70%-DKDP crystals with different orientations and varying laser intensities have been systematically analyzed at λ = 1064 and 532 nm. The results indicate that nonlinear absorption is not observed at λ = 1064 nm, but the phenomenon is very widespread at λ = 532 nm. Sample orientations and laser intensity are demonstrated to be essential factors in determining absorptive ability. In contrast to I- and II-type, z-directions for KDP and 70%-DKDP crystals show a relatively larger optical absorption. This means that I- and II-type samples, when used as frequency conversion devices, are more specifically suited to applications in high-power laser systems. The nonlinear absorption coefficients of KDP and 70%-DKDP range from 1.46×10^{-10} cm/W to 3.30×10^{-10} cm/W and 1.47×10^{-10} cm/W to 3.80×10^{-10} cm/W, respectively. A common feature is that nonlinear absorption coefficients increase first and then decrease with the increment of laser intensity for KDP and 70%-DKDP crystals. The characteristics of the nonlinear absorption effect and the calculated nonlinear optical parameters are extremely important in considering KDP and 70%-DKDP applications.

Acknowledgments: This work was supported by National Natural Science Foundation of China (No. 51321062 and 51602174) and Natural Science Foundation of Shandong Province (No. ZR2016EMQ04).

Author Contributions: Duanliang Wang and Shenglai Wang conceived and designed the experiments; Duanliang Wang wrote the paper; Jiyang Wang and Chuanying Shen contributed in the analysis of data and revision of the paper; Duanliang Wang, Weidong Li, Pingping Huang and Hui Liu performed the experiments and discussed the results; Robert I. Boughton contributed in revision of the paper including English and physics.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Liu, B.; Yin, X.; Sun, X.; Xu, M.; Ji, S.; Xu, X.; Zhang, J. Growth and electro-elastic properties of $K(H_{1-x}D_x)_2PO_4$ single crystals. *J. Appl. Cryst.* **2012**, *45*, 439–443. [CrossRef]
2. Li, T.L.; Zhao, X.H.; Zheng, Y.L.; Chen, X.F. Conical second harmonic generation in KDP crystal assisted by optical elastic scattering. *Opt. Express* **2015**, *23*, 23827–23833. [CrossRef] [PubMed]
3. Sharma, S.K.; Verma, S.; Singh, Y.; Bartwal, K.S. Growth technique to increase the device purpose yield of a KDP crystal and assessment of its quality using X-ray and optical techniques. *CrystEngComm* **2013**, *15*, 9955–9962. [CrossRef]
4. Liu, F.F.; Yu, G.W.; Zhang, L.S.; Li, L.; Wang, B.; Gan, X.Y.; Ren, H.K.; Zhou, H.L.; Zhu, L.L.; Ji, S.H.; et al. Effect of super-saturation on hillock of directional Growth of KDP crystals. *Sci. Rep.* **2014**, *4*, 1–5.

5. Cui, Z.J.; Liu, D.; Sun, M.Z.; Miao, J.; Zhu, J.Q. Compensation method for temperature-induced phase mismatch during frequency conversion in high-power laser systems. *J. Opt. Soc. Am. B* **2016**, *33*, 525–534. [CrossRef]
6. Ji, S.H.; Wang, F.; Zhu, L.L.; Xu, X.G.; Wang, Z.P.; Sun, X. Non-critical phase-matching fourth harmonic generation of a 1053-nm laser in an ADP crystal. *Sci. Rep.* **2013**, *3*, 1605. [CrossRef] [PubMed]
7. Guo, D.C.; Jiang, X.D.; Huang, J.; Wang, F.R.; Liu, H.J.; Xiang, X.; Yang, G.X.; Zheng, W.G.; Zu, X.T. Effects of γ-ray irradiation on optical absorption and laser damage performance of KDP crystals containing arsenic impurities. *Opt. Express* **2014**, *22*, 29020–29030. [CrossRef] [PubMed]
8. De Mange, P.; Negres, R.A.; Rubenchik, A.M.; Radousky, H.B.; Feit, M.D.; Demos, S.G. Understanding and predicting the damage performance of $KD_xH_{2-x}PO_4$ crystals under simultaneous exposure to 532- and 355-nm pulses. *Appl. Phys. Lett.* **2006**, *89*, 1–3.
9. Hu, G.H.; Zhao, Y.N.; Li, D.W.; Xiao, Q.L. Transmittance increase after laser conditioning reveals absorption properties variation in DKDP crystals. *Opt. Express* **2012**, *20*, 25169–25180. [CrossRef] [PubMed]
10. Schaffer, C.B.; Brodeur, A.; Mazur, E. Laser-induced breakdown and damage in bulk transparent materials induced by tightly focused femtosecond laser pulses. *Meas. Sci. Technol.* **2001**, *12*, 1784–1794. [CrossRef]
11. Li, F.Q.; Zong, N.; Zhang, F.F.; Yang, J.; Yang, F.; Peng, Q.J.; Cui, D.F.; Zhang, J.Y.; Wang, X.Y.; Chen, C.T.; et al. Investigation of third-order optical nonlinearity in $KBe_2BO_3F_2$ crystal by Z-scan. *Appl. Phys. B* **2012**, *108*, 301–305. [CrossRef]
12. Sheik-Bahae, M.; Said, A.A.; Wei, T.H.; Hagan, D.J.; Van Stryland, E.W. Sensitive measurement of optical nonlinearities using a single beam. *IEEE J. Quantum. Electron.* **1990**, *26*, 760–769. [CrossRef]
13. Wang, D.L.; Li, T.B.; Wang, S.L.; Wang, J.Y.; Wang, Z.P.; Ding, J.X.; Li, W.D.; Shen, C.Y.; Liu, G.X.; Huang, P.P. Effect of Fe^{3+} on third-order optical nonlinearity of KDP single crystals. *CrystEngComm* **2016**, *18*, 9292–9298. [CrossRef]
14. Messias, D.N.; Pilla, V.; Andrade, A.A.; Catunda, T. Nd:YAG optical electronic nonlinearity and energy transfer up conversion studied by the Z-scan technique. *Opt. Mater. Express* **2015**, *5*, 2588–2596. [CrossRef]
15. Ganeev, R.A.; Kulagin, I.A.; Ryasnyansky, A.I.; Tugushev, R.I.; Usmanov, T. Characterization of nonlinear optical parameters of KDP, $LiNbO_3$ and BBO crystals. *Opt. Commun.* **2004**, *229*, 403–412. [CrossRef]
16. Shaikh, R.N.; Anis, M.; Shirsat, M.D.; Hussaini, S.S. Investigation on the linear and nonlinear optical properties of L-lysine doped ammonium dihydrogen phosphate crystal for NLO applications. *J. Appl. Phys.* **2014**, *6*, 42–46.
17. Silambarasan, A.; Rao, E.N.; Rao, S.V.; Rajesh, P.; Ramasamy, P. Bulk growth, crystalline perfection and optical characteristics of inversely soluble lithium sulfate monohydrate single crystals grown by the conventional solvent evaporation and modified Sankaranarayanan–Ramasamy method. *CrystEngComm* **2016**, *18*, 2072–2080. [CrossRef]
18. Jin, L.T.; Wang, X.Q.; Ren, Q.; Cai, N.N.; Chen, J.W.; Li, T.B.; Liu, X.T.; Wang, L.N.; Zhang, G.H.; Zhu, L.Y.; et al. Preparation, characterization and third order nonlinear optical properties of the bis (tetrabutylammonium)–[Cd $(dmit)_2$] (dmit = 2-thioxo-1, 3-dithiol-4, 5-dithiolate) for all-optical switching applications at blue–green light band. *J. Cryst. Growth* **2012**, *356*, 10–16. [CrossRef]
19. Fan, H.L.; Wang, X.Q.; Ren, Q.; Li, T.B.; Zhao, X.; Sun, J.; Zhang, G.H.; Xu, D.; Sun, Z.H.; Yu, G. Third-order nonlinear optical properties in $[(C_4H_9)_4N]_2[Cu(C_3S_5)_2]$-doped PMMA thin film using Z-scan technique in picosecond pulse. *Appl. Phys. A* **2009**, *99*, 279–284. [CrossRef]
20. Wang, D.L.; Li, T.B.; Wang, S.L.; Wang, J.Y.; Wang, Z.P.; Xu, X.G.; Zhang, F. Study on nonlinear refractive properties of KDP and DKDP crystals. *RSC Adv.* **2016**, *6*, 14490–14495. [CrossRef]
21. Wang, D.L.; Li, T.B.; Wang, S.L.; Wang, J.Y.; Shen, C.Y.; Ding, J.X.; Li, W.D.; Huang, P.P.; Lu, C.W. Characteristics of nonlinear optical absorption and refraction for KDP and DKDP Crystals. *Opt. Mater. Express* **2017**, *7*, 533–541. [CrossRef]
22. Bhar, G.C.; Chaudhary, A.K.; Kumbhakar, P. Study of laser induced damage threshold and effect of inclusions in some nonlinear crystals. *Appl. Surf. Sci.* **2000**, *161*, 155–162. [CrossRef]
23. Cook, W.R., Jr. Thermal Expansion of Crystals with KH_2PO_4 Structure. *J. Appl. Phys.* **1966**, *38*, 1637–1642. [CrossRef]
24. Nelmes, R.J. Structural studies of KDP and the KDP-type transition by neutron and X-ray diffraction: 1970–1985. *Ferroelectrics* **1986**, *71*, 87–123. [CrossRef]

25. Liu, W.J.; Wang, S.L.; Gu, Q.T.; Ding, J.X.; Liu, G.X.; Sun, Y.; Liu, L.; Wang, B. Growth, structural and optical properties of 12%-deuterated KDP crystals. *Cryst. Res. Technol.* **2013**, *48*, 314–320. [CrossRef]
26. Pritula, I.; Gayvoronsky, V.; Gromov, Y.; Kopylovsky, M.; Kolybaeva, M.; Puzikov, V.; Kosinova, A.; Savvin, Y.; Velikhov, Y.; Levchenko, A. Linear and nonlinear optical properties of dye-doped KDP crystals: Effect of thermal treatment. *Opt. Commun.* **2009**, *282*, 1141–1147. [CrossRef]
27. Gurzadyan, G.G.; Ispiryan, R.K. Two-photon absorption peculiarities of potassium di-hydrogen phosphate crystal at 216 nm. *Appl. Phys. Lett.* **1991**, *59*, 630–631. [CrossRef]