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Effects of Thermal Annealing on the Optical Properties of the Potassium Dihydrogen Phosphate Measured Using UV-Vis-NIR Spectroscopy

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[#]*Equal Contribution*

Abstract

Potassium Dihydrogen Phosphate (KDP) crystals have been successfully grown under different conditions such as slow growth rate (2 mm/day), rapid growth rate (15 mm/day), and deuterium (80%) doping (DKDP). The extinction ratio, conductivity, absorption spectrum, laser damage threshold as well as optical scattering particles were fully investigated before and after thermal annealing in air, vacuum, N_2 and H_2, respectively. The correlations between optical properties and growth conditions were clarified. It was found that the laser damage threshold is proportional to the extinction ratio, optical transmittance, and however inversely proportional to the conductivity of the material. It was firstly convinced that the optical quality can be improved by thermal annealing in vacuum and H_2, and however no obvious effect in air and N_2.

Keywords

Potassium dihydrogen phosphate, Growth conditions, Optical properties, Thermal annealing

PACS

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Introduction

Potassium Dihydrogen Phosphate (KDP) and deuterium doped KDP (DKDP) crystals have been widely used in optoelectronics, information, and national defense due to the advantages of the rapid growth rate, high laser damage threshold, large electro-optic and nonlinear optical coefficients [1,2]. Study on the growth and various properties for (D) KDP crystals has lasted more than 90 years [3]. There are two problems which are urgent to be solved and one is the rapid growth of large-aperture (D) KDP crystals (more than 500 mm along *a* axis), and the other is about improvement of the optical and electrical qualities. Recently, 600 mm-aperture KDP has been obtained during two weeks, and therefore the first problem was basically solved [3,4]. Unfortunately, the second problem, especially for the improvement of the optical homogeneity and laser damage threshold has not yet been well solved by now [5,6]. The optical and electrical properties of (D) KDP crystals could be greatly affected by the growth rate, solution conditions, deuterium concentration and so on [7,8], and therefore study on the correlations between the growth conditions and optical properties may con-

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tribute to the improvement of the optical properties of (D) KDP. However, the changefulness of the growth conditions as well as numerous optical and electrical parameters of (D) KDP crystals made the correlation very complicated. In 2019, we designed and self-made a thermal annealing equipment, and simulated the temperature, stress distributions as well as airflow vectors in the equipment by the Finite Element Method [9]. This equipment has been used for annealing of all the (D) KDP samples on this study.

In this paper, the correlations between optical properties and growth conditions of (D) KDP were detailed clarified. Three growth conditions including traditional growth (1 ~ 5 mm/day), rapid growth (≥ 8 mm/day) and deuterium doped KDP(DKDP), as well as five optical parameters including extinction ratio, electrical conductively, transmittance spectra, laser damage threshold and distribution of the optical scattering particles, were taken into consideration[10]. In addition, the thermal annealing experiments in air, vacuum, N_2 and H_2 were also performed, and it was firstly found that the laser damage threshold is proportional to the extinction ratio, optical transmittance, and however inversely proportional to the conductivity of the material.

Experimental Section Z Tian

At first 20 samples were cut from KDP crystals grown from the three conditions with slow growth rate (2 mm/day), rapid growth rate (15 mm/day), and deuterium doping (80%), respectively. The (001) and (100) faces were polished, and a certain angle of each sample was chamfered in order to distinguish the ± *a* and ± *c* crystallographic directions. The samples were labeled as XYZ, Where X denotes the growth conditions such as slow growth rate (S), rapid growth rate (R) and deuterium doping (D), Y denotes the annealing conditions such as in air (K), vacuum (Z), N_2 (N), and H_2 (H), Z denotes the serial-number or crystallographic directions. For example, 1 ~ 8 means the measured order, and *a* or *c* refer to the crystallographic directions. The sizes and numbering of the 20 samples are shown as following: (a) 8 cuboid samples with sizes of 30 mm × 40 mm × 10 mm labeled as SK1, SK2, SZ3, SZ4, SN5, SN6, SH7 and SH8, along *a* and *c* directions respectively, were cut from KDP crystals with 2 mm/day growth rate. (b) 8 cuboid samples with sizes of 30 mm × 40 mm × 10 mm labeled as RK1, RK2, RZ3, RZ4, RN5, RN6, RH7 and RH8, along *a* and *c* directions, respectively, were cut from KDP crystals with 15 mm/day growth rate. (c) 4 cuboid samples labeled as DK1, DK2, DH7 and DH8, with size of 20 mm × 25 mm × 10 mm were cut from DKDP crystals. Then another unpolished 20 samples with sizes of 10 mm × 10 mm × 3 mm were cut from KDP crystals grown under above three conditions for measurements of their conductivity. They were labeled according to the above-mentioned rules. Finally, thermal annealing experiments were performed on all the samples in the atmosphere of air, vacuum, N_2 and H_2, respectively, from 50 °C to 200 °C. Then the extinction ratio, conductivity, absorption spectrum, laser damage threshold as well as optical scattering particles were measured and compared before and after annealing.

In this paper, the extinction ratio was described as Ei/Eo. Eo is the energy received after the analyzer, and Ei is the energy before the polarizer, which will be measured based on the reflected reference light. The extinction ratio is an important parameter for judging the quality of the KDP crystals. A large extinction ratio represents high optical quality. The conductivities were measured by using the conventional two-probe technique at room temperature. The absorption spectrum was measured by the UV-vis-NIR Spectroscopy. The laser damage threshold was measured by a Nd:YAG laser with a pulse width of 10 ns, and a repetition of 1 Hz at the working wavelength 1064 nm.

Results and Discussions

Measurements of extinction ratio

Five sites located at four corners and the central of each cuboid sample were selected to be measured. It was observed found that the measured extinction ratios are very different at different sites of each sample. The extinction ratios at central areas are generally higher than those at four corners, which indicate that the optical homogeneities in the center of the samples are better than that in edge areas. This is attribute to larger internal stresses which have been induced in the margin areas than in the center areas by the cutting and polishing processes. The comparisons of extinction ratios measured at different sites of each sample were shown in Figure 1a. In this figure F denotes the extinction ratio measured at the central, and B, C, D as well as E denotes the four corners of the samples. From Figure 1a, that the extinction ratios

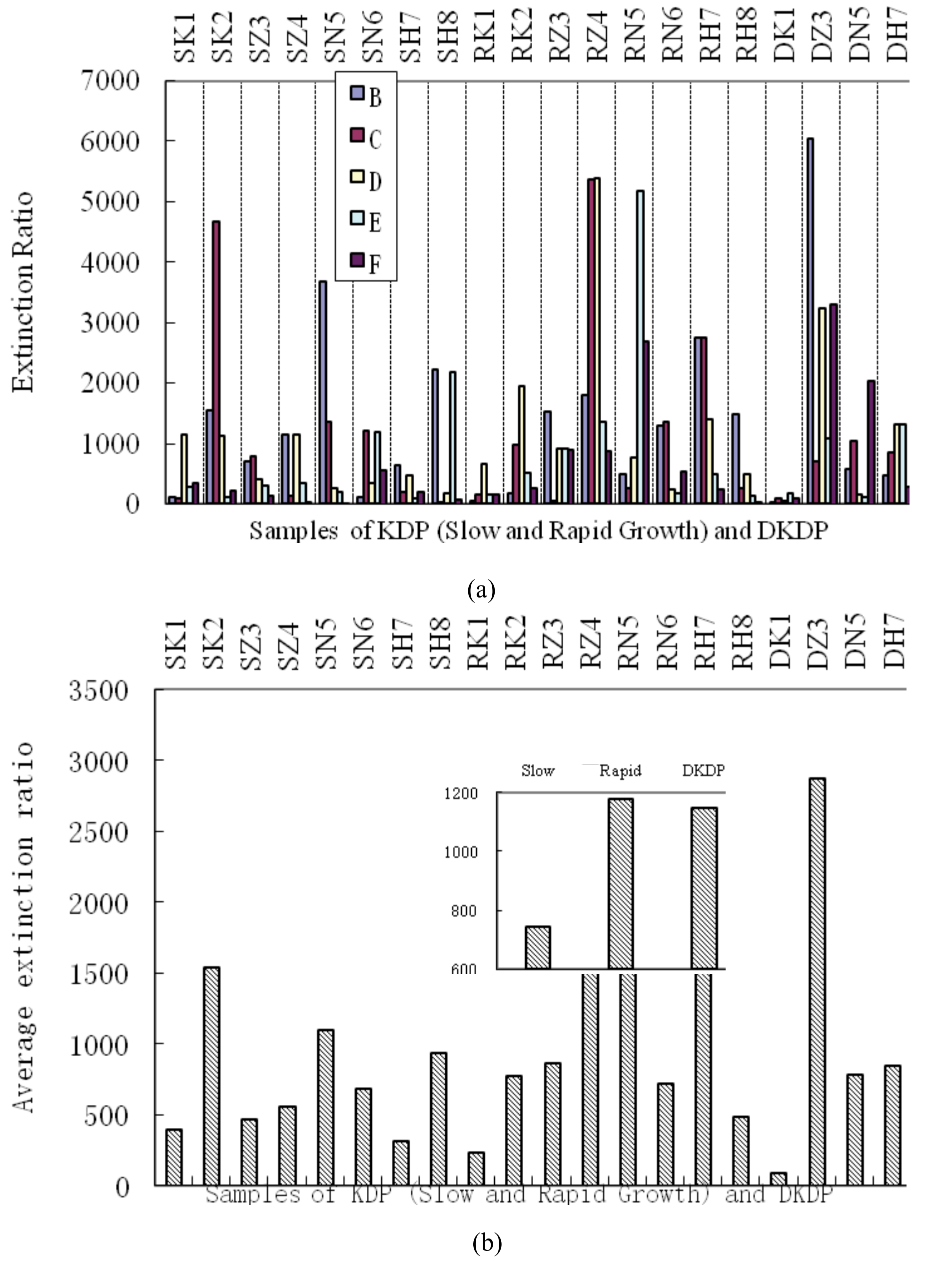

Figure 1: (a) The extinction ratio on different sites of slow or rapid grown KDP crystals; (b) The average extinction ratio on different 5 sites of each KDP crystal. The inset shows the extinction ratio of slow and rapid grown KDP and DKDP.

of crystals labeled as SK1, SK2 and SZ4 are lower than 350 at four corners, and higher than 1000 at the center of the samples. The trend of extinction ratios of the eight samples with rapid growth labeled as R** is upwards, and most of the measured values are larger than 1000. The random distribution of the extinction ratios appears on the four DKDP crystals, and for instance five measured extinction ratios of the DK1 sample are very low, and whereas very high for DZ3. Neglecting the difference of extinction ratios located at different areas in one sample, the values out to compare the optical homogeneities of crystals with different growth conditions was averaged and Figure 1b shows the average extinction ratio on different 5 sites of each sample. It was seen From Figure 1b that the optical homogeneities of crystals labeled as SK1, SK3, SK4, SN6, SH8, RK1, RH8 and DK1 are worse, that is to say, 5 traditional growth, 2 rapid growth and 1 DKDP crystals appear worse optical qualities and their extinction ratios are lower than 500. Here it was noted that the optical qualities could be different due to sample processing although all the samples were cut from one crystal. So again, the average of 8 traditional, 8 rapid growth KDP and 4 DKDP crystals, and the results were shown in the inset of Figure 1b.

From the inset it can be learned that the average extinction ratio of crystals with traditional growth conditions is 746, the rapid growth KDP is 1178, and DKDP is 1146, which indicates that the optical homogeneities of rapid growth KDP and DKDP are better than traditional growth KDP. This result is obvious against common sense because it is generally believed that the optical quality would be perfect when the crystals growing with slow rate and high-purity. These measurement results also indicate that the effects of growth conditions on the qualities of DKDP crystals are very complicated, and one parameter is not enough to characterize the optical qualities of this crystal. So, the measurement results of other optical or electrical parameters of all samples will be given next.

Conductivity

The conductivities of all the samples were measured along *a* and *c* direction, respectively, using the conventional two-probe technique at room temperature. The results were shown in Figure 2. The conductivities along *a* direction of five KDP crystals (62.5% of all KDP samples) labeled as SK, SZ, SH, RN and RH, and three DKDP crystals (75% of all DKDP samples) labeled as DZ, DN and DH, are larger than those along *c* directions. The conductivities of 4 traditional, 4 rapid growth KDP and 4 DKDP crystals were averaged and shown in Figure 2. It could be observed from this Figure that the conductivities were ranked in order of traditional growth KDP > rapid growth > DKDP. The conductivities along *a* directions of rapid growth KDP and DKDP crystals were larger than those along *c* directions, while for traditional growth KDP crystals, it was just the opposite. So, we drew a conclusion that the conductivities of DKDP crystals along *a* direction are usually larger than those along *c* directions since the electron transport channels are main along *a* direction. In addition, it was noted that the extinction ratios of traditional growth KDP crystals are the lowest but their conductivities are whereas highest, and the extinction ratios of DKDP are larger but the conductivities are whereas lower. The results indicated that the extinction ratio is approximately inversely proportional to the conductivity of the samples.

Optical transmittance

Transmittance spectra of all samples were measured along *a* and *c* directions, respectively and shown in Figure 3. It can be seen that the whole transmittance range can be divided into four spectral regions, such as 200 ~ 400 nm (I), 400 ~ 850 nm (II), 850 ~ 1200 nm (III) and 1200 ~ 1800 nm (IV).

For region I, the transmittances of DKDP and traditional growth KDP were higher than those of rapid growth KDP, and they were ranked in order of traditional growth KDP (measuring along *c* di-

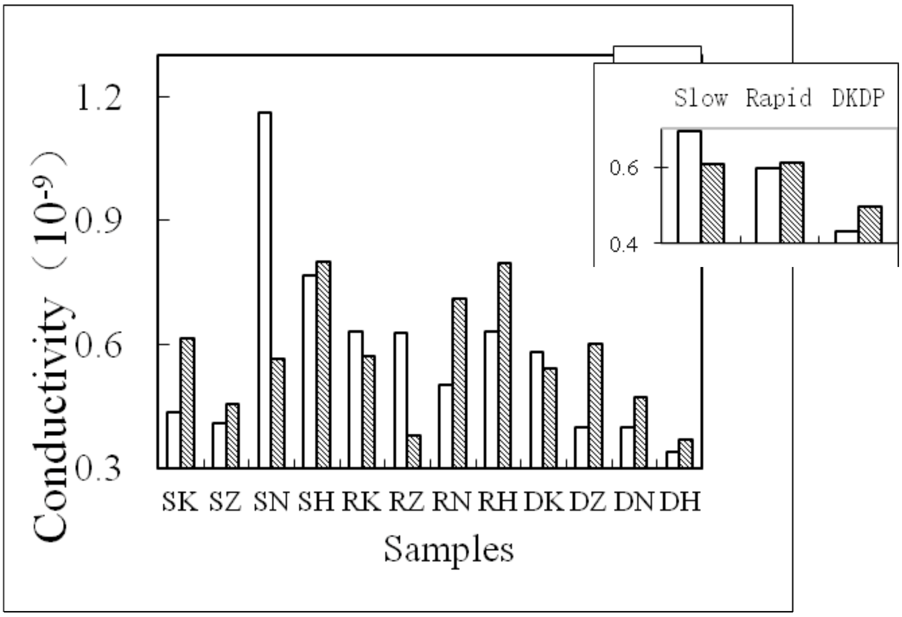

Figure 2: Conductivity of traditional, rapid growth KDP and DKDP crystals.

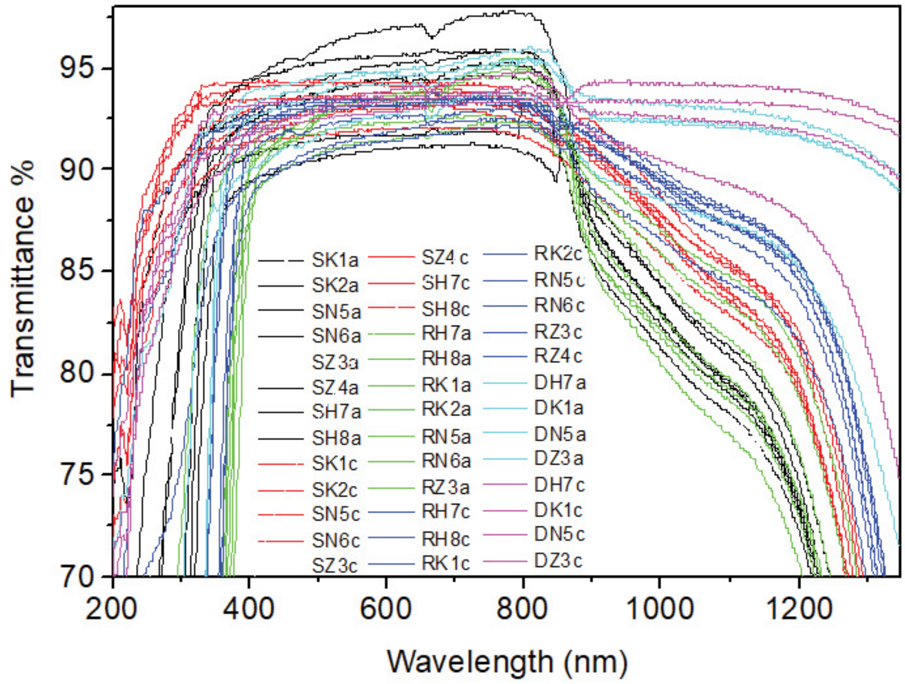

Figure 3: The transparent spectra of slow and rapid KDP and DKDP.

Table 1: Laser induced damage of KDP and DKDP crystals.

Samples	Energy(mJ)	Energy density(J/cm^2)	Power density(GW/cm^2)
DN5	192 ~ 240	24.4 ~ 30.6	2.44 ~ 3.06
DH7	240	30.6	3.06
RH7	95 ~ 143	12.1 ~ 18.2	1.21 ~ 1.82
RK2	143	18.2	1.82
SK2	220	28	2.8
SK1	143 ~ 200	18.2 ~ 25.5	1.82 ~ 2.55

rections) > DKDP (along *c* directions) > traditional growth KDP (along *a* directions) > DKDP (along *a* directions) > Rapid growth KDP (along *c* directions) > Rapid growth KDP (along *a* directions). For region II, the average transmittance of all samples is higher than 90%, and they were ranked in order of DKDP (along *a* directions) > DKDP (along *c* directions) > traditional growth KDP = Rapid growth KDP. We note that an inflection point appeared at about 850 nm for all samples, except for DKDP measuring along *c* direction. Regarding III, the average transmittance of all samples except for DKDP is lower than 90%, and they were ranked in order of DKDP (along *c* directions) > DKDP (along *a* directions) > Rapid growth KDP (along *c* directions) > traditional growth KDP (along *c* directions) > Rapid growth KDP (along *a* directions) = traditional growth KDP (along *a* directions). For region V, the transmittances of KDP decrease sharply, while for DKDP decrease slowly to 80% at about 1500 nm and then fell sharply too. The results indicated that the average transmittance of traditional growth KDP is higher as we expected than those of rapid growth KDP, which however seems to be inconsistent with the measured extinction ratios. In other words, the higher the transmittance is, the lower the measured extinction ratio. It was suggested that the optical properties could be well characterized by transmittance than extinction ratio since the extinction ratio is more sensitive to the micro defects, sample orientations or other factors, whereas the transmittance reflects macro and statistical effect.

Laser damage threshold

The beam diameter was minimized by a lens system to 1 mm. The measured results were listed in Table 1. From this table it can be seen that the laser damage threshold of DKDP is highest up to 240 mJ.

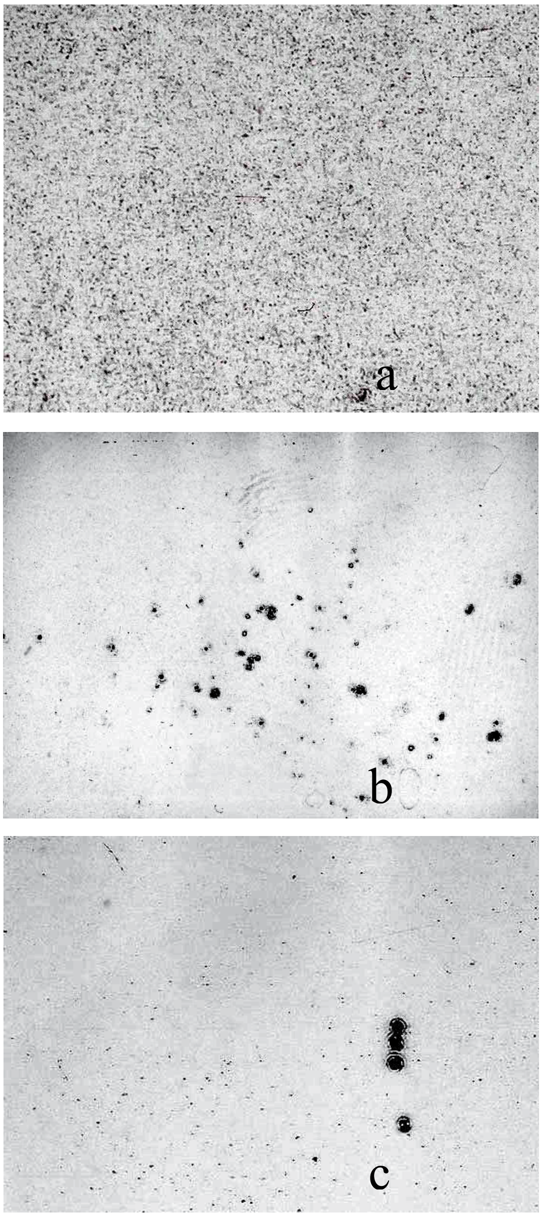

Figure 4: Scattering particles observed in typical: (a) Traditional; (b) Rapid growth KDP and; (c) DKDP crystals.

The values of rapid growth KDP are obvious lower than those of DKDP and traditional growth KDP and the highest is only up to 143 mJ. Combined with above measured other optical or electrical parameters, it was found that the laser damage threshold is approximately proportional to the extinction ratio, optical transmittance, and whereas inversely proportional to the conductivity.

Distribution of optical scattering particles

Figure 4a, Figure 4b and Figure 4c shows the photographs of scattering particles observed in typical traditional, rapid growth KDP and DKDP crystals. From Figure 4a it could be learned that the density of optical scattering particles in traditional growth KDP is very high although the sizes are small, which may be responsible for lowing of the above measured extinction ratios. The density of scattering particles in rapid growth KDP as shown in Figure 4b is low and the distribution is somewhat localized although the sizes are relatively large, which leading to the accidental influence on the extinction ratio measuring. From Figure 4c it was noted that the density of scattering particles in DKDP is very low although the sizes are 2 ~ 5 times larger than that of rapid growth KDP crystals, indicating that the right extinction ratios could be obtained if the incident beam avoids the scattering particles.

In addition, all the samples were thermal annealed in air, vacuum, N_2 and H_2, and then the extinction ratio, conductivity, absorption spectrum, laser damage threshold as well as optical scattering particles were measured and compared before and after annealing. It was found that the optical quality can be improved by thermal annealing in vacuum and H_2, and whereas no obvious effect in air and

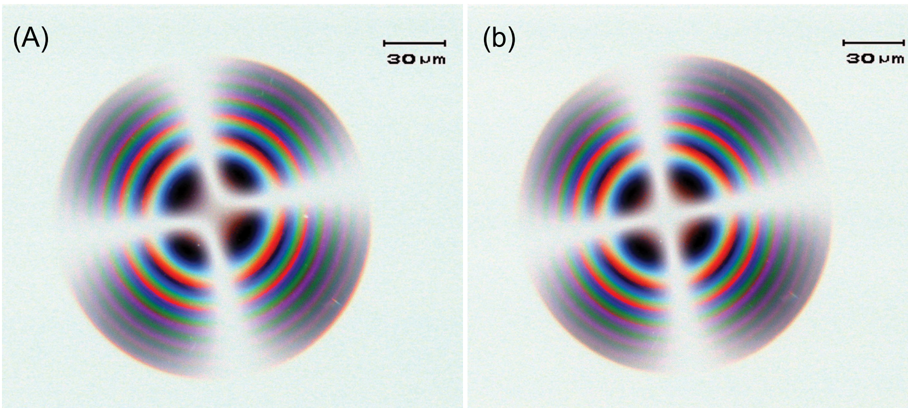

Figure 5: Taper optical interference at the edge of KDP crystals before and after H_2 annealing.

N_2. As an example, the taper optical interference patterns observed in the edge of typical traditional growth KDP before and after thermal annealing in H_2 were shown in Figure 5. It is obvious that the internal stress in crystals decreased by H_2 annealing and the optical quality is therefore improved. The similar results for other optical and electrical parameters have also been obtained, and in this paper the detailed descriptions were omitted.

Conclusions

The optical and electrical measurements, including the extinction ratio, conductivity, absorption spectrum, laser damage threshold as well as optical scattering particles, were performed on the traditional, rapid growth KDP and DKDP crystals, respectively. The thermal annealing in air, vacuum, N_2 and H_2 were also performed on all samples. The effect on optical properties of growth conditions and the correlations among various optical parameters were investigated. It was concluded that the laser damage threshold is approximately proportional to the extinction ratio, optical transmittance, and whereas inversely proportional to the conductivity, and we firstly found that the optical quality can be improved by thermal annealing in vacuum and H_2, and whereas no obvious effect in air and N_2.

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