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Impurity and Laser-Induced Damage in the Growth Sectors of Rapidly Grown KDP Crystals

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ABSTRACT

We report the experimental results of impurity contamination and laser-induced damage investigations on rapidly grown potassium dihydrogen phosphate (KDP) crystals. Using absorption spectroscopy and chemical analysis, we determind the impurity distribution in the different growing sectors of KDP single crystals. The level of impurity was dependent on the starting materials and growth rate. We also studied the influence of impurities on the laser-induced damage in fast grown KDP. The laser damage threshold in the impurity-rich prismatic sector is same as in the high purity pyramidal sector within the experiemntal error. Meanwhile, the laser damage threshold (LDT) at the boundary of the prismatic and pyramidal sectors is less than half of that in the bulk. Furthermore, we found that the thermal annealing of the crystal eliminated the weakness of this sector boundary and increased its LDT to the same level as in the bulk of the crystal. Our result suggests that laser damage occured in the vicinity of a high, localized strain field.

Keywords: impurities, laser induced damage, KDP, crystals

1. INTRODUCTION

KDP single crystals are commonly used nonlinear optical materials for harmonic generation of laser radiation[1]. Large (40x40 cm^2) KDP crystals with high damage thresholds are required for high power laser applications, such as the National Ignition Facility[2]. Conventionally, KDP crystals with sizes longer than 20 cm have been grown from saturated aqueous solution at growth rates of about one millimeter per day along the primary optical (z) axis. Recently[3], large KDP crystals have been grown successfully from highly supersaturated solution at rates exceeding 10 mm per day. In addition to the growth of the pyramidal faces (along the z axis), as occurs in the conventional method, rapid crystallization from supersaturated solution results in significant growth of prismatic faces in directions (x,y) perpendicular to the primary optical axis. As a result, material from the two growth sectors typically contains different levels of impurities. In this report, we summarize our efforts to correlate the optical properties of the crystals with the presence of chemical impurities in the prismatic and the pyramidal growth sectors. We also performed laser-induced damage threshold (LDT) studies on the two different growth sectors as well as at their boundaries both before and after thermal annealing. The results address the issue of optical performance and laser induced damage in KDP crystals.

2. ULTRAVIOLET ABSORPTION AND IMPURITY ANALYSIS

Figure 1 shows the ultraviolet (UV) absorption spectra of a KDP crystal fabricated from a rapidly grown boule and cut perpendicular to the z-axis. The absorption spectra were measured along the z axis and show a dramatic spatial variation because of the impurity distribution. The central spot (Figure 1[a]) lies in the pyramidal sector, while two spots near the edge (Figure 1[b,c]) are in the prismatic sector. As the figure shows, the absorption in the pyramidal sector is much lower in magnitude and has different spectrum from that of the prismatic sector. The spectral analysis shows that the absorption in the prismatic sectors commonly consists of bands at 200 and 270 nm. However, the relative intensities of the two bands vary dramatically with position. Figure 2 shows the absorption spectra of two plates cut from the same boule of KDP, but at different heights along the z-axis. The position at which the 200-nm absorption increases in magnitude is nearer to the outer edge in #5-3 than in #5-2, consistent with the shift at the pyramid-prism sector boundary position as the crystal grows taller. Therefore, the absorption at 200 nm primarily depends only on the growth sector in which it is measured. However, the 270-nm absorption band (monitored at 300 nm to resolve it more fully from the 200-nm band) also depends on the relative growth rates of the crystal. Unlike the 200-nm band, whose absorption is constant in the prismatic sector, the 300-nm absorption in both plates increase monotonically with the growth rate, as shown in

Figure 2. Also, the higher magnitude of both absorption bands correlates with higher impurity contamination in the crystals, as measured by inductively coupled plasma-mass spectrometry (ICP-MS), as discussed below.

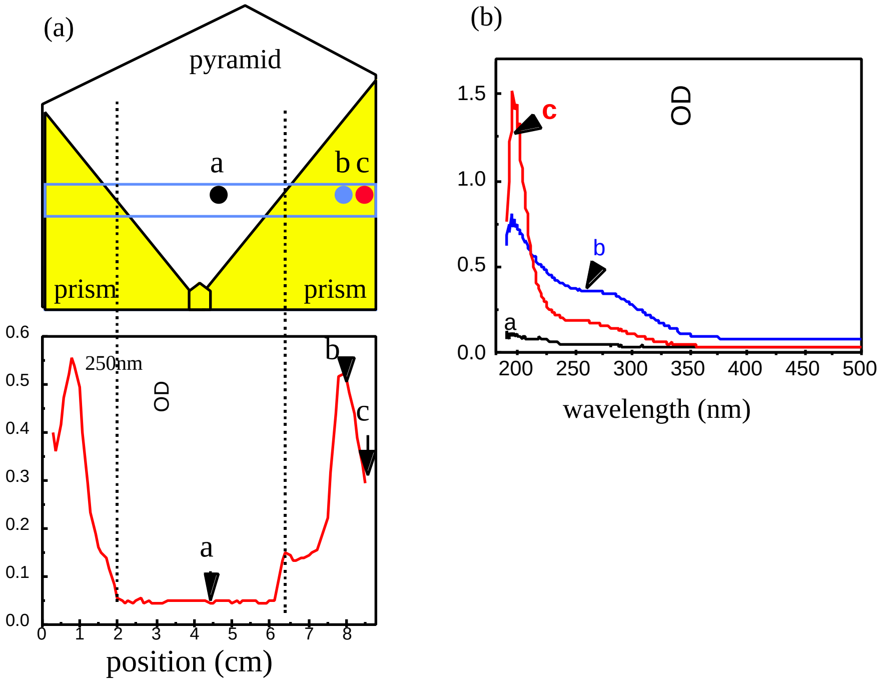


Figure 1. (a) Schematic diagram of KDP crystal boule and location of crystal plates measured. The open area is the pyramidal sector and shaded one is the prismatic. The bottom shows the spatial variation in optical absorption at 250 nm (same horizontal scale as above). (b) The absorption spectra at position a, b and c as shown in (a)

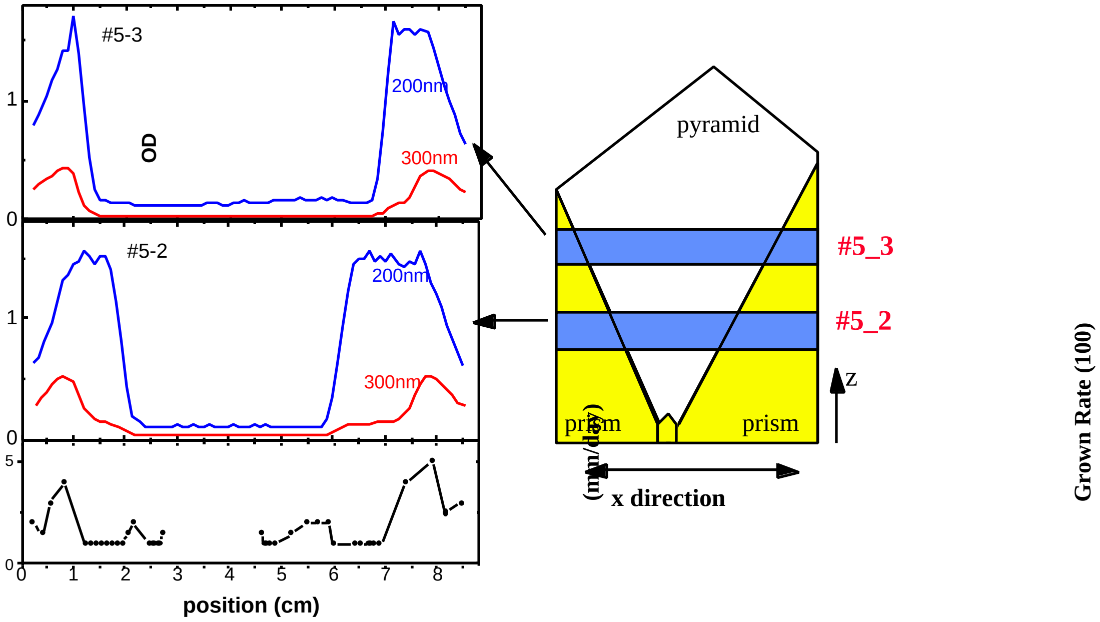


Figure 2. The absorption spectra of the top (#5-3), the bottom (#5-2) plate, and their growth rate as a function of position along the x direction.

Besides of the critical loss of the laser intensity at the 355 nm wavelength, the UV absorption also correlates with degredation of the optical performance, such as distortion of the transmitted wavefront and birefringence loss. Figure 3 shows a comparison the spatial profiles of UV absorption with the level of strain induced optical birefringence as measured by depolarization loss. The strong correlation indicates that the incorporation of impurities is one cause of optical distortion that affects the quality of crystals used for harmonic generation.

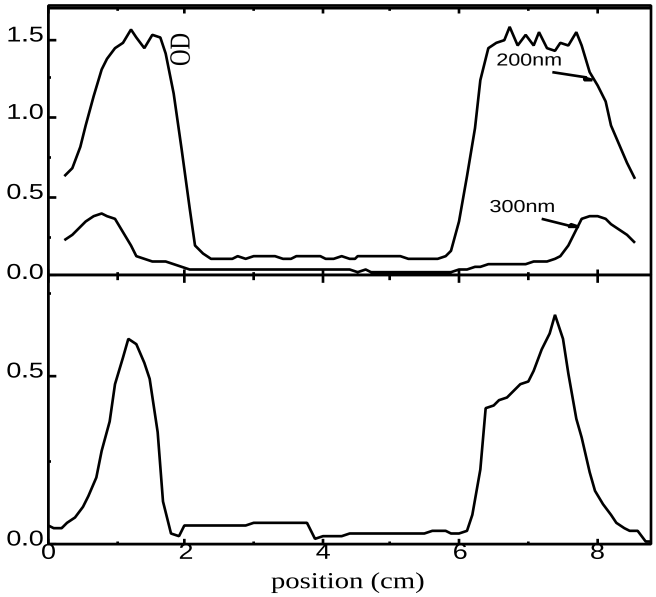


Figure 3. The absorption and depolarization loss in crystal #5-2 as a function of position.

Chemical analyses using ICP-MS show that impurities in KDP are at the parts per million level. Table 1 lists analytical data for the KDP crystals referred to above. The data show that the segregation of impurities from the starting solution to the crystal is different in the two growth sectors, and also depends on the identity of the individual impurities. The ratio of impurity concentrations in the prismatic and pyramidal sectors were measured by secondary ion mass spectroscopy (SIMS) analysis using micrometer- size $^{16}O^-$ primary ion beam. Higher concentrations of aluminum, chromium, iron, strontium, yttrium, zirconium, antimony, barium, silicon, lanthanum, and cerium were found in the prismatic sector, magnesium is enriched in the pyramidal sector and rubidium remains relatively constant between two sectors.

impurity ions	starting salts (ppm	LLNL 5-2 pyramid (ppm)	LLNL 5-2 prism (ppm)	SIMS analysis prism/pyramid
Sb (Antimony)	3.5	0.17	12.5	150-500
Pb (Lead)	0.2	0.1	0.2	-
Al (Aluminum)	<0.6	<0.3	7	30
Fe (Iron)	<0.2	<0.06	0.6	100-200
Rb (Rubidium)	3.8	0.8	0.8	1

Table 1. Impurity analysis of KDP salt and different growth sectors

The origin of the observed impurity-induced UV absorption is not yet fully understood. We have found that the absorption at 200 and 270 nm is also present in the starting aqueous solutions and that the absorption at 270 nm increases in the solution as the impurity level increases. Our initial intentional doping experiments show that insoluble metal phosphates have the same absorption spectrum as observed in the starting solutions and final crystals. Such molecular impurities may be responsible for the UV absorption we measured. However, a more complete understanding of the UV-absorption due to each impurity requires more experiments where the presence of impurities are individually controlled.

3. LASER INDUCED DAMAGE AND THERMAL ANNEALING

The damage tests were performed using a Q-switched Nd:YAG laser with 10 Hz operation at 355 nm (3ω) and a 7.6 ns pulse width. The damage laser fluence was typically varied from 2 to 25 J/cm^2 with 1.1 mm beam diameter. The laser induced damage was inspected using a 100X darkfield microscope before and after laser irradiation. In addition, a scatter diagnostic laser was used to illuminate the test site and was co-aligned with the damaging beam. A CCD camera with 10μm resolution was used to collect the scattered light at 90° to the incident laser direction[4].

Figure 4 shows the results of standard laser-induced damage threshold (LDT) measurements with 600 shot exposures (S:1 damage test) in the prismatic and pyramidal sectors. This standard test shows that the laser damage threshold remains at the same level in both sectors in spite of large variations in impurity content between these two growth sectors. This observation contradicts other published data[5] which shows that higher UV absorption results in a lower LDT. However, this is the first time the measurement of LDT with impurity (UV absorption) variations have been measured in the same crystal. We also performed high fluence tests on those sites that survived the initial standard test. The damage threshold increases almost two-fold when the site was pre-irradiated. The conditioned S:1 threshold is just a two step fluence ramping comparing with standard R:1 test with multiple step fluence ramping. This is consistent with the laser conditioning effect observed in earlier work[5].

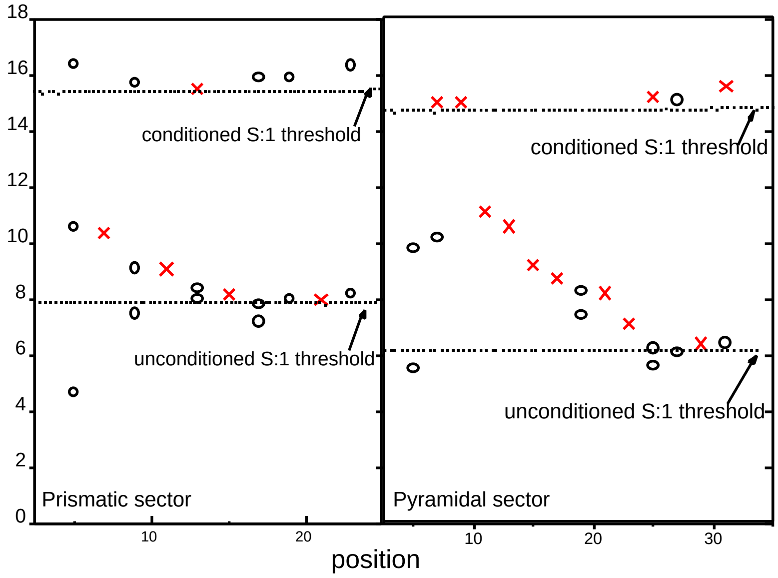
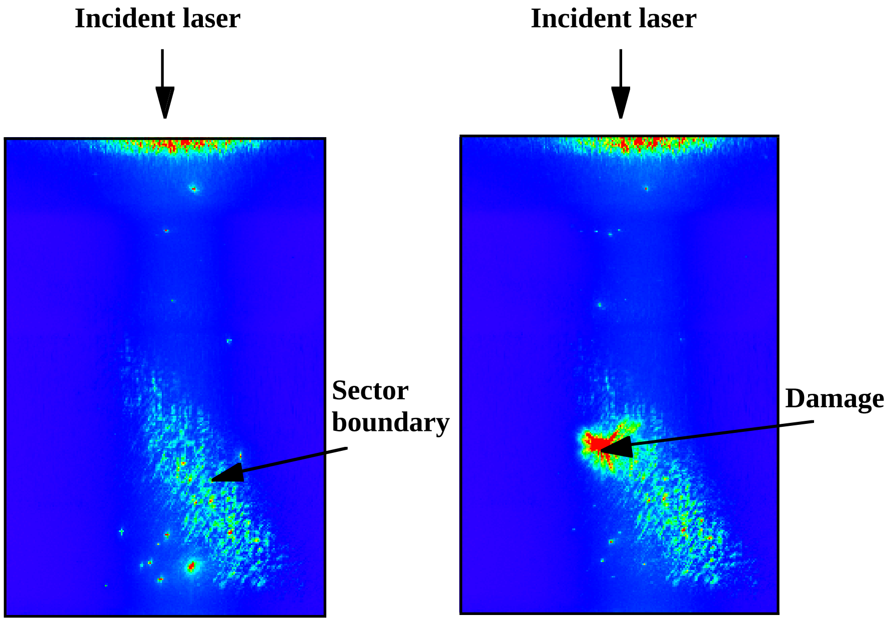


Figure 4. The laser-induced damage threshold as a function of position in (a) pyramidal and (b) prismatic sectors. Circles represent sites that survived the damage test, while crosses represent sites where we observed damage. The sites with more than one symbol were tested at low fluence before testing at high fluence.

In addition, we found the LDT of the prism-pyramid sector boundary was only 2 to 3 J/cm^2, which is less than half of that in the bulk of the crystal. Figure 5 shows the light scattering from the sector boundary before and after laser irradiation. A laser fluence of 9.7 J/cm^2 caused catastrophic sector boundary damage which was a few hundreds of micrometers in size and observable by the naked eye. The pre-irradiation image shows intense light scattering due to the strain in the sector boundary where the catastrophic damage occurs. Furthermore, both the sector boundary scattering and LDT were not altered by laser annealing (preirradiation).



Before damage **After 600 shots at 7J/cm^2**

Figure 5. Images of scattered light from pyramid/prism sector boundary before (left) and after (right) laser irradiation at 7J/cm^2 fluence. Damage and diagnostic laser were incident at the top of the image, and the images were collected at 90^0 to the direction of the incident beam. The intense scattering in the images at roughly 45^0 angle is from the sector boundary.

Following the initial testing, the crystals were annealed in a vacuum oven at 160 C for approximately 120 hours. *After thermal annealing, the intense light scattering from the sector boundary was no longer observable and the LDT along the sector boundary increased dramatically to the same level as the LDT in the bulk of the crystal.* The disappearance of light scattering at the sector boundary suggests that strain at the boundary was thermally annealed, thereby increasing the damage threshold. These observations also suggest that the laser damage occurs in the vicinity of a highly localized strain field. The localized strain could distort chemical bond or could enhance local electrical field and result in higher optical absorption to cause material breakdown. The UV absorption in the bulk of the crystal after thermal annealing was measured and remains the same as before annealing. This suggests that the UV absorption is not due to those crystal defects that can be thermally annealed, such as those generated by irradiation,. Currently, we have not been able to directly correlate impurity segregation with damage at the sector boundary because of the spatial resolution in the measurement. The standard LDT test in pyramidal and prismatic sectors performed after thermal annealing showed no significant increase in the LDT, which differs from the case of laser-induced damage at 1ω irradiation[6].

In summary, we measured the impurity content in two growth sectors of rapidly grown KDP single crystals. The level of contamination depends on the starting materials and the growth rate. The impurities observed by absorption spectroscopy are identified as the origin of lattice distortion and anomalous optical birefringence in the KDP crystals. We also found that the laser damage threshold of highly impure prismatic sectors is the same as that of the high purity pyramidal sectors. The laser damage threshold at the sector boundary is at least twice as low as in the bulk of the crystals. We have successfully thermally annealed the crystal defects along the sector boundary and increased the boundary LDT to the same level as in the bulk crystal.

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4. REFERENCE

1. D. Eimerl, *Ferroelectrics*, **72**, 95 (1987) and papers in the same volume.
2. J. Campbell, *ICF Quarterly Report* 5(1), Lawrence Livermore National Laboratory, Livermore, CA UVRL-LR-105821-95-1 (1994)

3. N.P. Zaitseva, I.L. Smol'skii, and L.N. Rashkovich, *Sov. Phys. Crystallogr*. **36**, 113 (1991)
4. M. Runkel, B. Woods, M. Yan, J. De Yoreo and M. Kozlowski, *SPIE*, **2714**, 185 (1995)
5. M.I. Kolybaeva, I.M. Pritula, V.M. Puzikov, V.I. Salo, S.V. Garnov and S.M. Klimentov *SPIE* proceedings, **2114**, 46 (1993)
6. L.J. Atherton, F. Rainer, J.J. De Yoreo, I.M. Thomas, N. Zaitseva and F. De Marco, S*PIE proceedings*, **2114**, 36 (1993)

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