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Abstract

Interest in producing high-damage-threshold KH_2PO_4 (KDP) and $(D_xH_{1-x})_2PO_4$ (DKDP) (also called KD*P) for frequency conversion and optical switching applications is driven by the requirements of the National Ignition Facility (NIF) at the Lawrence Livermore National Laboratory (LLNL).[1] At present only the best crystals meet the NIF system requirements at the third harmonic (351nm) and only after a laser conditioning process. Neither the mechanism for damage in bulk KDP nor the mechanism for conditioning is understood. As part of a development effort to increase the damage thresholds of KDP and DKDP, we have been developing techniques to pinpoint the locations where damage will initiate in the bulk material. After successfully developing a diagnostic tool that will find these locations, we will use other measurement techniques to determine how these locations differ from the surrounding material and why they cause damage. This will allow crystal growers to focus their efforts during the growth process in improving damage thresholds.

Previously we reported that there was a low correlation between defects in crystals located using light scatter and the sites where damage would initiate.[2] Damage, when it occurs, is almost certainly associated with a localized heating of the crystal which results in mechanical damage to or chemical decomposition of the crystal lattice. If this heating occurs at fluences below the damage threshold, we should be able to measure this heating and predict the locations where damage will initiate prior to damaging the crystal. As a result, we are developing photothermal (PT) techniques to probe the bulk material to look for heating due to localized absorption and to determine the correlation between localized heating and the initiation sites for damage.

This paper reviews the current status of our photothermal work on KDP.

Keywords: KDP, DKDP, bulk damage, photothermal deflection

1. Introduction

KDP will be utilized as the electro-optic material in a large aperture Pockels cell used in the multipass architecture employed on the NIF as well as for the second harmonic converter. DKDP is utilized for the third harmonic converter in order to suppress stimulated Raman scatter.[3] The operating fluence of the NIF is limited by bulk damage to the KDP and DKDP, specifically, damage to the third harmonic conversion crystal at 351nm. Damage threshold requirements for each of these components and current damage threshold performance of both conventionally grown and rapid grown crystals were reported last year in these proceedings.[2]

Damage in KDP has always occurred at isolate sites which leads us to believe that local defects of some type are responsible for initiating damage. Our efforts to locate these defects using light scattering techniques were largely unsuccessful.[2] When damage occurs it is almost certainly preceded by localized heating, the question is if at fluences below the damage threshold is this localized heating present and can we measure it. Photothermal measurements have been used for many years to measure very small absorptions on surfaces, in coatings and in bulk materials and solutions.[4,5,6,7] We have implemented a photothermal absorption measurement to study localized absorptions, to generate three-dimensional absorption maps of the bulk material, and to determine a correlation between these maps and the initiation sites for damage. We began our experimental effort by determining if we could measure photothermal absorption signals in bulk material of KDP. After successfully measuring photothermal signals in KDP, we proceeded to determine if there were measurable differences in the signals between different crystals with different growth histories and if there were differences in the signals within a single crystal. We found there were indeed differences between crystals and within a single crystal. We then proceeded to construct an experiment that would generate three-dimensional photothermal absorption maps that show localized variations in the absorption. Currently we are optimizing our measurement system, looking into repeatability issues, and determining if a correlation exists between the photothermal absorption maps and initiation sites for damage.

2. High-Fluence Photothermal Deflection Experiment

Figure 1 is a schematic of the high-fluence photothermal deflection experiment. The experiment incorporates a pulsed frequency-tripled YAG for the pump beam with a 3ns pulsewidth at 355nm operating between 10 and 100Hz. It is focused to about 30µm diameter inside of the sample. The probe beam, a diode laser operating CW at 780nm, is normal to the surface of the crystal and is focused to 80µm diameter inside of the sample. The beams intersect at nominally 45° and are offset slightly in the vertical direction such that thermal lensing is detected as a vertical movement of the probe beam on the position-sensitive detector. The beams crossing at an oblique angle allow us to probe the thermal lensing only in the interaction region where the pump and probe beams cross giving us the ability to do three-dimensional mapping of the absorption of the sample. The sample is affixed to a computer controlled X Y Z translation stage which is moved in order to probe different locations in the sample. Output from the position sensitive detector is amplified, and sum and difference signals between quadrants are achieved using operational amplifier circuitry. The output can then be recorded using an oscilloscope, a lockin amplifier, or boxcar integrators.

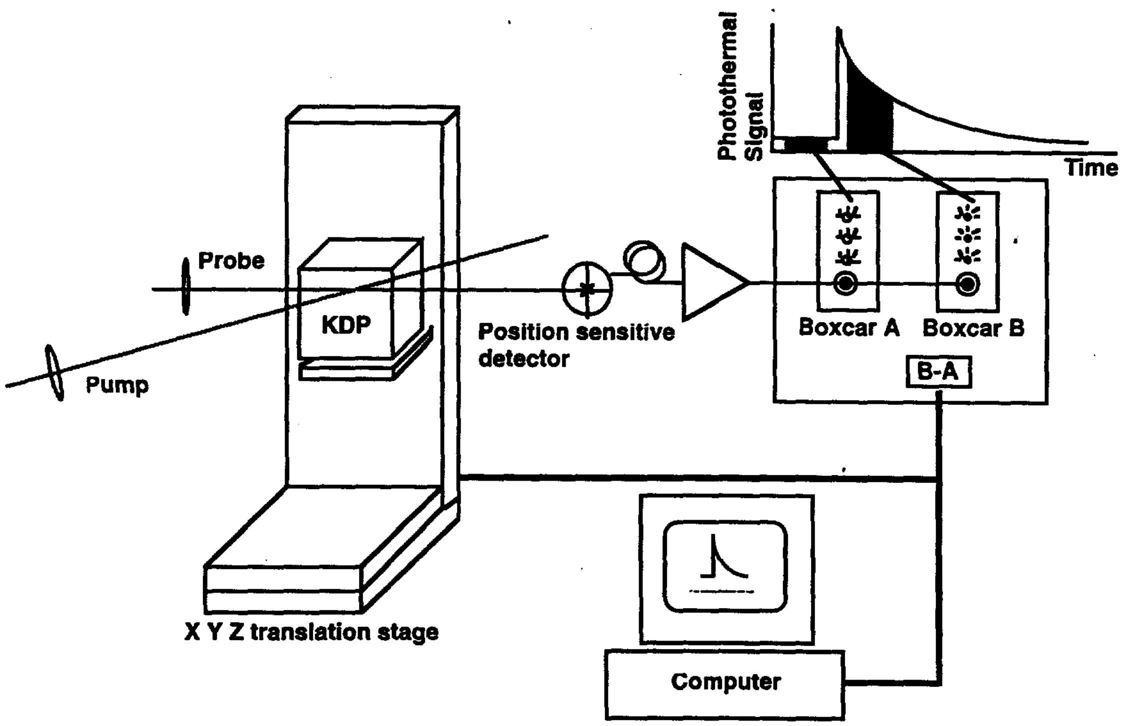

Figure 1. Experimental Layout

The output from the position sensitive detector was initially observed using a digitizing oscilloscope to determine if we could measure a photothermal signal in KDP. A typical photothermal deflection signal is shown in Figure 2. The pulsed pump beam is incident on the sample at t=0 seconds on the plot. We were able to detect reasonable signals in KDP. We increase signal to noise by averaging a number of consecutive shots with the oscilloscope.

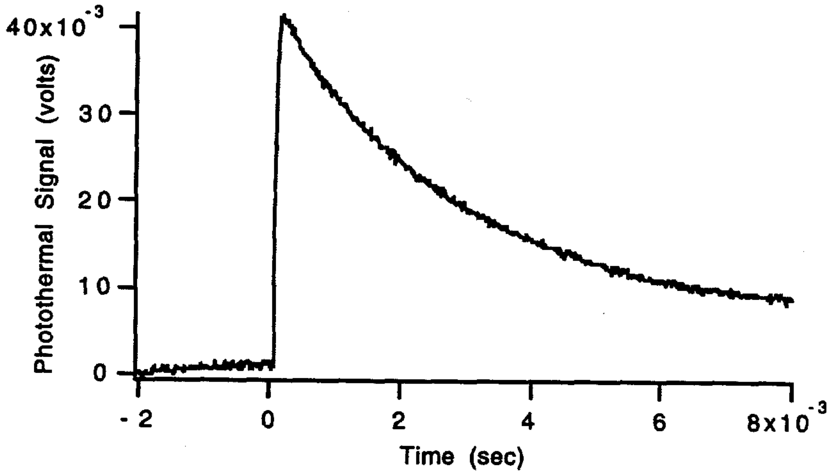

Figure 2. Typical photothermal signal from KDP. The photothermal signal represents a movement of the probe beam on the position sensitive detector.

The photothermal signal was measured as the intensity of the pump beam was varied. Figure 3a shows a series of time resolved photothermal signals as the intensity of the pump beam was increased. Note that the photothermal deflection signal exhibits a millisecond decay time which is consistent with the thermal diffusion in KDP crystals. The peak amplitude of the photothermal signal plotted as a function of the intensity of the pump beam is shown in Figure 3b and was found to vary as the square of the pump intensity. This suggests that the absorption and thus the heating is due to a two-photon absorption process. Because the energy of two photons at 355nm is smaller than the energy of the band-gap in KDP, the observed absorption must be caused by defect states. In addition, the two-photon absorption varies with crystal quality.

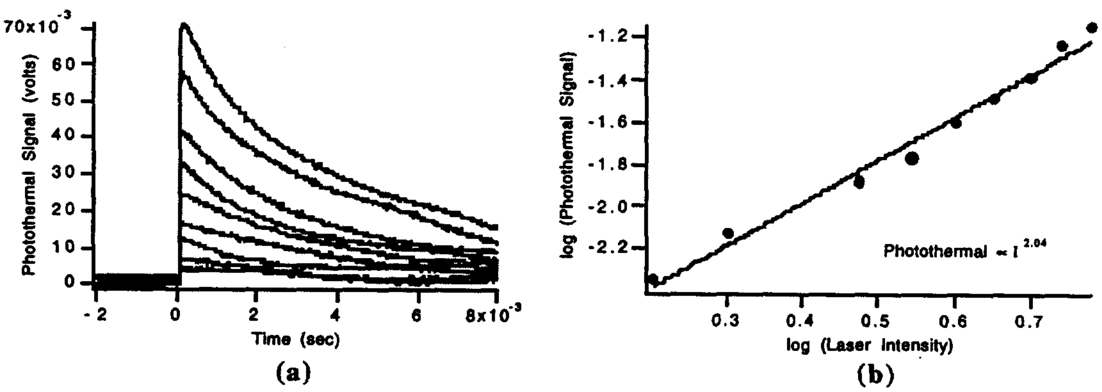

Figure 3. Photothermal signal for KDP: a) Photothermal signals for increasing pump beam intensities. b) Peak photothermal signal versus pump intensity shows a two-photon absorption process.

To make absolutely certain that the photothermal deflection signal would vary linearly with the incident laser intensity in the absence of two-photon absorption, a neutral density (ND) filter with low absorption was tested. The peak amplitude of the photothermal signal when plotted as a function of the intensity of the pump beam exhibited a very linear behavior for the ND filter as shown in Figure 4. This measurement also allowed us a means of correlating our photothermal signals to an absolute absorption using the ND filter as a known calibrated standard.

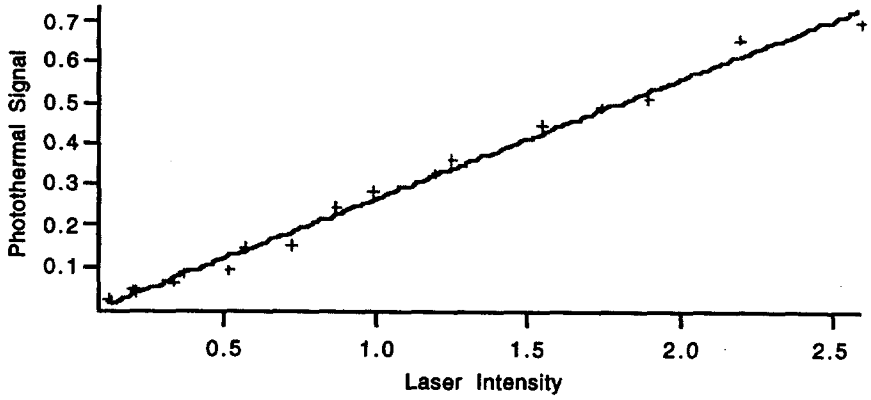

Figure 4. Photothermal signal for ND filter.

Having shown that we could measure photothermal signals in KDP, we focused our attention on determining whether we could see differences within a crystal and differences crystal to crystal. It has been shown[8] that the segregation coefficients for impurities that we believe could play a role in lowered damage thresholds for KDP are much higher for the prismatic material than for the pyramidal material, in some cases as much as 10 to 20 times higher. Pyramidal growth is that which occurs on the (101), $(\bar{1}01)$, (011), and $(0\bar{1}1)$ facets. Prismatic growth is that which occurs on the (100) and (010) faces as shown on the inset of Figure 5. The result is a higher linear absorption at 355nm in the prismatic sector.[8] Figure 5 shows the photothermal signal within a single crystal for both pyramidal and prismatic material. The photothermal signal in the prismatic material is larger than in the pyramidal material by about a factor of two which supports the conclusion that the two-photon absorption process in KDP is a result of impurities incorporated into the crystal. The cause of a high two-photon absorption due to impurity defects is still unclear, however, a band gap state resulting from impurities would lie inside of the wide band gap of KDP. Such a state is an electronic trapping center in the crystal and acts as a heating source. The decay of the photothermal signal fits a single exponential very well with the decay time for the pyramidal material being about 25% less than that of the prismatic material. There are two possible explanations for this difference in decay times. First, the thermal diffusivity of the material has been modified by the incorporation of impurities. The second and most likely reason is that the decay of electronic trapping states due to impurities is different for the prismatic and pyramidal material. The heat which is generated due to the decay of these trapping states reflects this difference.

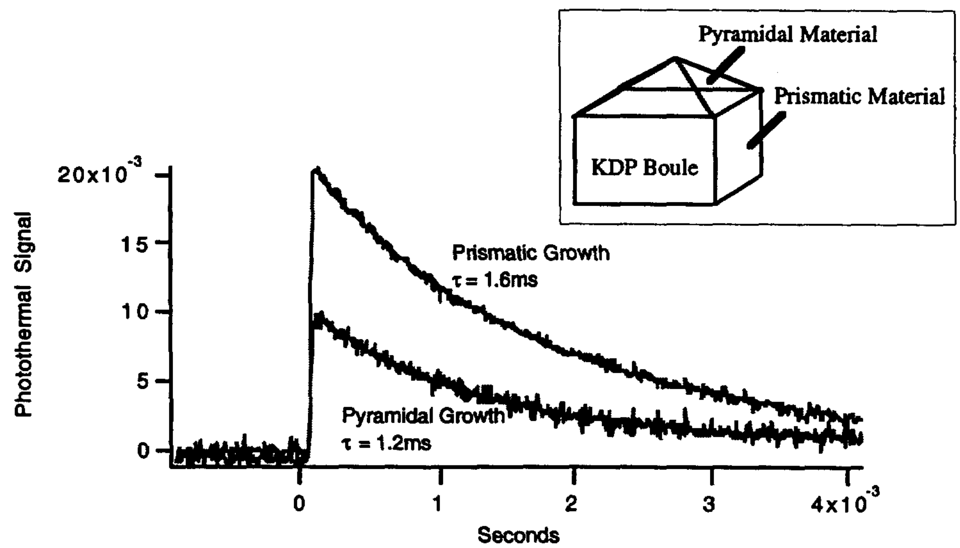

Figure 5. Photothermal signals for prismatic and pyramidal material within a single crystal.

Besides seeing differences in photothermal signals between prismatic and pyramidal material, we have also observed differences between crystals grown in different ways, with different growth parameters and different impurity levels. Figure 6 summarizes some of the differences we have seen amongst various crystals. The Beamlet KDP, which was grown by conventional processes, had the lowest photothermal signal, the lowest concentration of impurities, and the highest damage threshold Several rapid grown crystals which were intentionally doped with impurities showed moderate to high photothermal signals. This suggests that impurity incorporation and/or localized stresses in the crystal can reduce the band gap in KDP the result of which is higher two-photon absorptions.

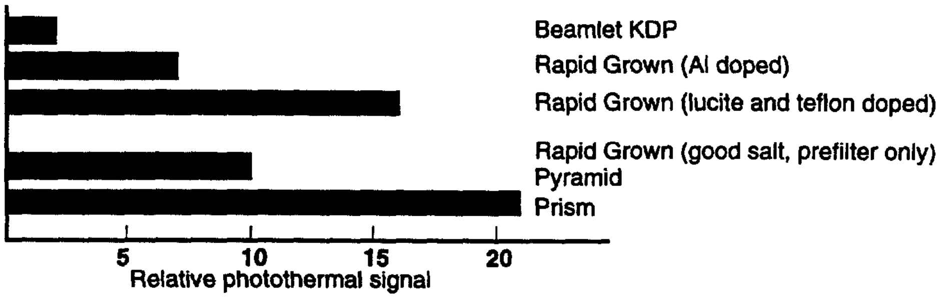

Figure 6. Photothermal signals for various crystals.

In order to study long term stability and repeatability, the output of the position sensitive detector was connected to a lockin amplifier and displayed on a strip chart. Figure 7 shows an example of the time history of the photothermal signal for a KDP sample that was doped with aluminum. In general these experiments showed long term stability, repeatability, and a signal to noise level that was adequate to allow us to see differences in photothermal signals site to site within a single crystal. This is evident in the data for sites 1 and 2 in Figure 7. One intriguing aspect of the long term behavior of this sample is that when a site is illuminated, initially it has a several minute decay time over which the signal comes to a steady state value. This phenomena is repeated at each new site as shown for the initial illumination of sites 1 and 2. When a site is irradiated again after the initial time there is no long term decay, even if it has been several days since the site has been irradiated. It is interesting to note that this is the only crystal, of those tested, which exhibited this type of behavior.

Figure 7. Long term photothermal signals measured using lockin techniques (1 horizontal division = 1 minute).

An automated system was implemented that would allow us to measure the photothermal signal and map out a volume of a sample (see Figure 1). The output from the position sensitive detector in this experiment was input to two channels of a boxcar integrator, one of which integrates a portion of the baseline before the pump pulse and the other which integrates a portion of the signal after the pump pulse. The difference between these two signals is taken to normalize for steering of the beam due to variations in the sample and the result is stored in a data file. The result is absorption maps such as that shown in Figure 8. Figure 8 is a three-dimensional photothermal map of a rapid grown crystal 3000 X 3000 X 6000μm at 100 X 100 X 100μm resolution. The map clearly shows the difference in absorption between the prismatic and pyramidal sections and is quite repeatable scan to scan. Estimates using a calibrated reference sample result in absorptions of about 4%/cm for the prismatic region and of about 1%/cm for the pyramidal region.

Although we have only recently began to produce three-dimensional photothermal absorption maps, to date we have not produced maps which show repeatable small localized variations in either the pyramidal or prismatic regions of a crystal. Maps such as those in Figure 8 show variations in the average absorption of the interaction region of the pump and probe beams but do not show localized variations that we believe are important in the laser damage process. Our experimental geometry is not currently optimized to detect the size and absorption levels of inclusions that we feel are responsible for damage in KDP. Light scatter measurements that were conducted on KDP[2] should show defects that are roughly a micron or larger yet we found these defects were not typically responsible for damage. We have also found that the damage threshold for single crystals which have both pyramidal and prismatic growth is essentially the same even though the level of impurities are much higher in the prism than in the pyramid. Currently our growth solutions are filtered to 20nm using a constant filtration process during growth. This information suggests that evenly dispersed impurities as well as large micron size inclusions are not typically responsible for damage in KDP. Filtration of the growth solution suggests that collections of impurities on the order of tens of nanometers and smaller in size would not be filtered from the solution and could be initiation sites for damage. Calculations[9] show that optical absorption could be enhanced by such nanometer sized particles or precipitants. The localized heating due to absorption by nanometer-sized particles or clusters of defect states could result in damage either through mechanical fracture due to thermal stress, destruction due to the tetragonal to monoclinic phase transition near 200°C, or local melting.[10]

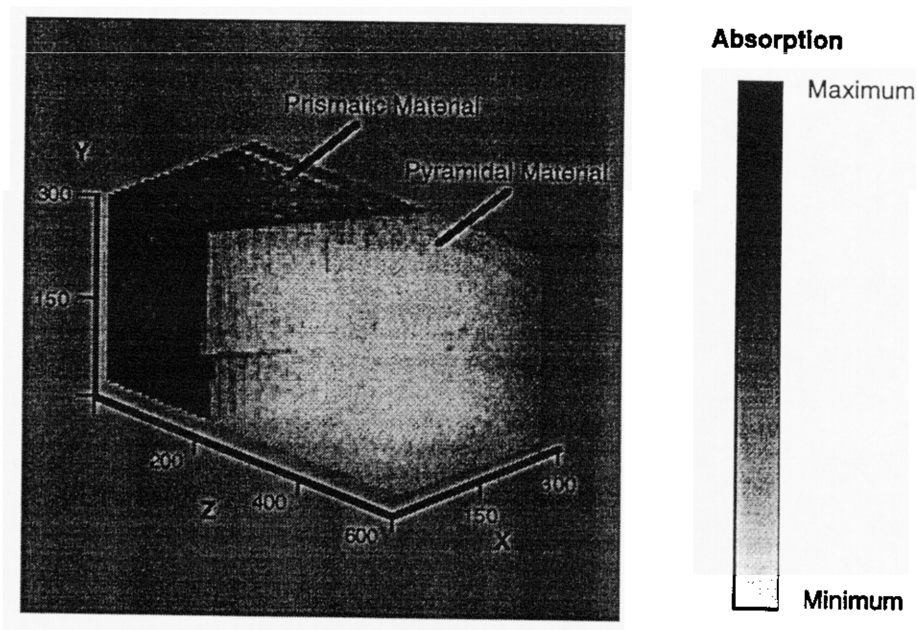

Figure 8. Three-dimensional photothermal map for a rapid grown crystal showing a dramatic difference in absorption between prism and pyramidal material.

3. Conclusions

We have seen photothermal deflection signals in KDP and have detected differences in these signals between different crystals and within a single crystal. The photothermal absorption signal at 355nm is due mostly to a two-photon absorption process in which impurities or stress lowers the band gap energy. Photothermal absorption signals are large enough and our measurement signal to noise is such that we are able to detect variations within a single crystal and crystal to crystal. The signals typically do not change over long time periods of time, but we did observe in one crystal a several minute decay over which the photothermal signal reached steady state. We have developed the capability to produce three-dimensional photothermal absorption maps in bulk materials and have produced initial maps showing a clear differences between the bulk absorption in the prismatic and pyramidal sectors of the crystal.

Currently we are reconfiguring our experiment to produce three-dimensional photothermal maps that show small variations in the local absorption that we feel may correlate to initiation sites for damage. In order to do this our experimental geometry must be optimized and the signal to noise ratio must be large enough to detect localized heating from particles that are on the order of tens of nanometers and whose absorption coefficients are approximately 10^4 times larger than the background absorption of KDP. Since KDP has a reasonably large two-photon absorption coefficient, it would be difficult to detect absorptions from small inclusions above the background. This may motivate us to pursue measurements using a CW pump since its linear absorption is small in KDP at 355nm.

4. Acknowledgments

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5. References

1. National Ignition Facility Conceptual Design Report, Vol. 2 and 3, Lawrence Livermore National Laboratory, Report No. UCRL-PROP-117093, May 1994.
2. B. Woods, et. al., "Investigation of Damage in KDP Using Light Scattering Techniques," Laser Induced Damage in Optical Materials, SPIE 2966, 20-31 (1996).
3. C. E. Barker, R. A. Sacks, B. M. Van Wonterghem, J. A. Caird, J. R. Murray, J. H. Campbell, K. R. Kyle, R. B. Ehrlich, and N. D. Nielsen, "Transverse Stimulated Raman Scattering in KDP," in First Annual International Conference on Solid State Lasers for Application to Inertial Confinement Fusion, Michel Andre, Howard T. Powell, Editors, Proc. SPIE 2633, (1995).
4. S. E. Bialkowski, *Photothermal Spectroscopy Methods for Chemical Analysis*, J. D. Winefordner ed., John Wiley and Sons, Inc., New York, (1996).
5. "The Thermal Lens in Absorption Spectroscopy," Ultrasensitive Laser Spectroscopy, D. S. Klinger ed., 175-232, Academic Press, New York (1983).
6. W. B. Jackson, N. M. Amer, A. C. Boccara, and D. Fournier, "Photothermal deflection spectroscopy and detection," Applied Optics, 29, 1333-1344 (1981).
7. Z. L. Wu, P. K. Kuo, C. Stolz, "Photothermal characterization of optical thin films," Optical Engineering, **36**(1), 9-12 (1997).
8. M. Yan, R. Torres, M. Runkel, B.W. Woods, I.D. Hutcheon, N. Zaitseva, and J.J. DeYoreo "Investigation of impurities and laser induced damage in the growth sectors of rapidly grown KDP crystals" SPIE, vol. 2966, 11, 1997.
9. Mike Feit, private communication.
10. J. Grunberg, S. Levin, I. Pelah, and D. Gerlich, "High temperature phase transitions and metastablility in KDP type crystals" Phys. stat. sol. (b) 49, 857 (1972)

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