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# Laser Induced Material Modification in the Bulk KDP Crystals

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# Laser induced material modification in the bulk KDP crystals

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**ABSTRACT**

Laser induced material modifications in the bulk and on the surface of KDP ($KH_2PO_4$) and DKDP (70-80% deuterated KDP) are studied using fluorescence imaging and spectroscopy. Photoluminescence is observed at damaged regions following above threshold exposure with an emission peak centered at 550-nm In addition, surfaces exposed to >100 high power, 355-nm laser pulses reveal a reduced surface finishing quality as evidenced by an associated emission under UV photoexcitation. The emission spectra from the laser-induced damage sites and the laser degraded surfaces are similar suggesting the generation of similar defect species.

**Key words:** Damage, KDP, Material modification, Spectroscopy

## 1. INTRODUCTION

A significant limitation on the operating fluence of high peak power lasers is the laser damage threshold of the optical components. The design of UV laser systems, including the final optics package for the National Ignition Facility (NIF) laser [1], is limited to a large extent by the laser damage performance of the third harmonic generator, which is made from deuterated potassium dihydrogen phosphate (DKDP) [2]. The damage may occur either in the bulk of the material or on the surface. In the past, the surface damage threshold of KDP and DKDP crystals was usually higher than the bulk damage threshold for diamond-turned surfaces. However, as the bulk damage threshold increased over time, primarily in response to better filtration of growth solutions and purer salts, the surface damage problem became more obvious.

Damage morphology is strongly suggestive that light-absorbing initiators deposited throughout the crystal during growth "explode" when exposed to sufficient fluence, thereby forming a melted and fractured zone a few micrometers in diameter. Laser-induced damage can be discussed in terms of two key issues: damage initiation by some type of precursor and damage growth due to subsequent laser pulses. In the first case, absorbing sub-micron in size particles that may be trapped during crystal growth or induced at the surface of the crystal during the polishing process can absorb laser energy, heat and expand, thereby thermally and mechanically stressing the surrounding host material which can lead to mechanical material damage [3.4]. The need to understand the factors that can affect the performance and lifetime of optical components for high peak power lasers, require development of techniques that can detect and characterize the light absorbing damage initiation centers and their behavior before and after interaction with high-power laser pulses.

This work is an effort to better understand the surface and bulk damage limitations of KDP crystals arising from material modifications due to the interaction with high power, 355-nm laser pulses. We report our investigation on light absorbing defect formations and material modifications due to this interaction. High fluence, below damage threshold, near-UV laser irradiation on the surface of 70-80% deuterated $KH_2PO_4$ crystals held in a low vacuum environment can introduce a sufficient defect population on the surface that can change the macroscopic optical properties of the material. During the damage process, the host material near and at the damage site is submitted to extreme conditions. The result of this process is that the material at the damage site is modified from its original crystalline structure and its optical properties become very different to that of the perfect crystal. The spectroscopic investigation of the material modifications and laser induced defect formations was carried out using micro-spectroscopy and microscopic fluorescence imaging.

## 2. EXPERIMENTAL SET-UP

The experimental arrangement is shown in fig. 1. The third harmonic of a 3-ns pulse-width, Q-switched, Nd:YAG laser is overlapped with the CW output of an argon laser operating at 351-nm. The two overlapped and collimated beams are propagating along the z-axis, (optical axis of the crystals investigated), and in bulk investigation the beams are focused using a 7.5 cm focal length fused silica cylindrical lens. For surface characterization, the 351-nm laser beam of the argon laser is focused using the 7.5 cm cylindrical lens on the surface of the sample at a grazing angle (see fig. 2) for the acquisition of high resolution fluorescence images of optically active defect formations. For bulk imaging, the imaging system is positioned perpendicular to the x-z plane of the crystal. A detailed description of the imaging system has been reported previously [5,6]. In brief, the imaging system used in this investigation is composed of X20 microscope objective followed by a X5 magnification zoom.

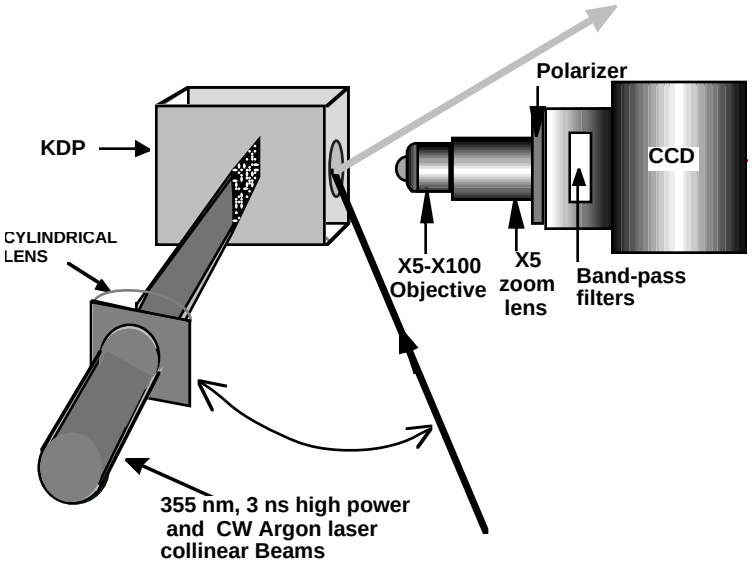



**Figure 1.** Schematic diagram of the experimental setup to study surface and bulk defect formations using microscopic fluorescence imaging

lens. The images were recorded using a liquid nitrogen cooled CCD detector. The imaging plane of the imaging system is overlapped with the focal plane of the cylindrical lens that delivers both the 355-nm damaging and the CW argon 351-nm illumination probe sources. This arrangement allows for microscopic imaging of CW illuminated areas and ensures correlation with material changes arising by the damaging 355-nm source. Optical filters are positioned between the CCD and the zoom lens to discriminate the Raman signal and the scattering illumination light and allow propagation through the filter only of these photons emitted at the imaged area that are confined in a particular spectral band. The samples investigated were fast-grown KDP and DKDP crystals. The experiments were performed with the sample held at room temperature.

## 3. RESULTS

DKDP samples, 5cmX5cmX1cm in size, polished by single-point diamond flycutting were exposed, within a vacuum chamber at room temperature and a pressure of $10^{-5}$ Torr, to 355 nm, 12 ns, laser pulses using below damage threshold fluences. The laser beam illuminated a 3mm x 4mm (approximately) section of the sample with a near uniform in intensity (rectangular) beam profile. Care was taken to ensure that the laser beam did not intersect any part of the test apparatus to become a possible source for contamination during the experiment. Handling of the parts through irradiation was done in a clean environment. Following irradiation, samples were brought to atmospheric pressure and spectroscopic measurements were performed using a 351 nm CW Argon ion laser for excitation. The microscopic fluorescence imaging system shown in fig. 1 was employed to obtain information on the spatial distribution of the photo-generated defects and a 5-μm spatial resolution spectroscopic system

was used to acquire the emission spectral characteristics of these defects. Fig. 2a shows a microscopic fluorescence image (in the 450-1050 nm spectral region) of a 1mmX1mm section at the surface of a sample that was irradiated with 1000 pulses having average energy per pulse of ~4 J/cm$^2$. Fig. 2b shows the light scattering image of the same location. The irradiated regions are offset to the right in each image to include area unexposed to laser irradiation for comparison and enhancement of the image contrast. The irradiated parts of the sample are clearly delineated in both images. The fluorescence image indicates that the surface of the crystal is modified under exposure to a relatively small number of high fluence, UV laser pulses and it contains a large defect population. Experiments performed using various laser irradiation levels and number of pulses indicate that even a small number of pulses (less than 100) can lead to the formation of defects without a visible degradation of the surface finishing quality. However, for a large number of pulses, the surface finish is also degrading and appears to the naked eye as gray haze. This is shown in the light scattering image of fig. 2b. The emission intensity from the irradiated area of the sample monotonically increases as a function of the number of pulses and laser fluence. Fig. 3 shows the emission spectrum in the 400-750 nm spectral region of the surface defect population generated in vacuum conditions under exposure to high power 355-nm pulses below damage threshold. The spectral characteristics of the emission was measured using the 351-nm laser beam of an argon laser to photoexcite the sample. A reflecting microscope objective was used to focus the laser beam into the sample and collect the emitted light. This configuration offers spatial resolution of ≈5μm.

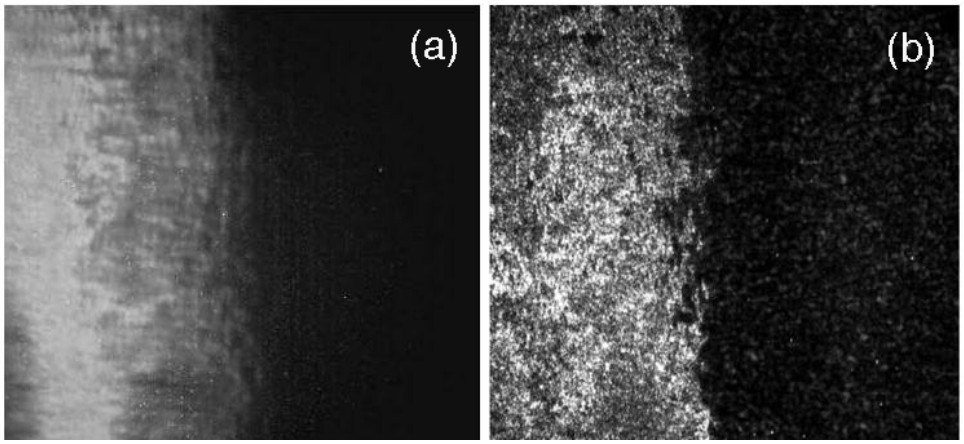
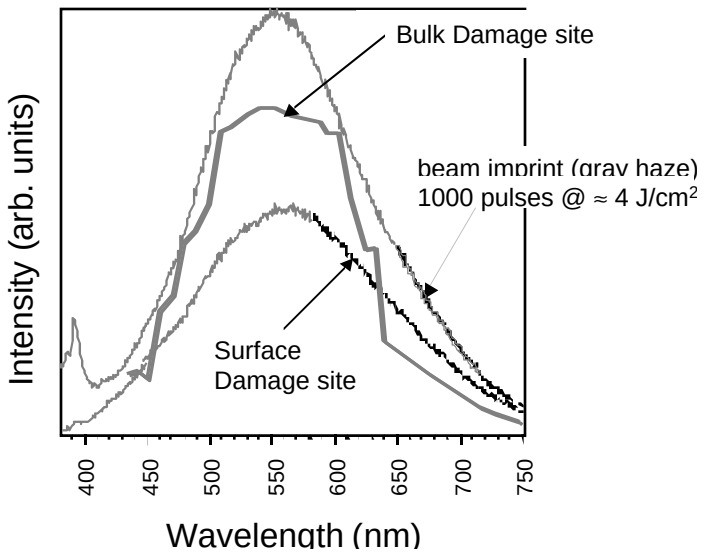



**Figure 2**: a) Microscopic fluorescence image in the 450-1050 nm spectral region and b) light scattering image of the of an 1mmX0.8mm section at the surface of a $KD_2PO_4$ sample that was irradiated with 1000 pulses at ~4 J/cm$^2$.

Laser induced damage is accompanied with a characteristic emission indicative of plasma formation. High temperature and stress are build up in the localized environment of the damage site within the pulse duration and relaxes within tens of msec. thereafter. The damage site morphology is evident of this violent process. The changes in the optical properties of the material at damage site in the bulk as well as at the surface of KDP and DKDP crystals were investigated using the experimental setup shown in fig. 1.

Figs. 4a and 4b show emission images of the same 600X600X25 μm$^3$ section inside the bulk of a KDP



crystal following two and three 355-nm pulses with above damage threshold fluences. These images show the initiation and evolution of damage sites within the bulk of KDP using for imaging the emission of defects generated during the damage process. These images as well as a set of experiments we have carried out using the same approach reveal a number of interesting findings.

Comparison of images of damage sites obtained using light scattering and fluorescence

**Figure 3**: Emission spectra in the 400-750 nm spectral region from the irradiated part of the surface of KDP at below damage threshold illumination in vacuum and from defects populations at damage sites in the bulk of KDP and the surface of DKDP crystals.

imaging reveal that all damage sites exhibit emission. This indicates that the damage process leads to the generation of defects with electronic structure well bellow the bandgap of the host crystal. The structure of a damage site as seen in the emission image contains very localized high intensity sites and an area around these high intensity sites which exhibits significantly less emission. The experimental results also demonstrate that for the fluences used in this experiment (estimated to be 8±4 J/cm$^2$), a number of bulk damage sites exhibits increase in their size and propagate in space as a result to exposure to additional 355-nm pulses.

The emission spectra from damage sites located in the bulk of KDP crystals is shown in fig. 3. The spectrum was constructed by recording images of the same crystal damaged section using narrow-band filters through the spectral range of 450-800-nm in increments of 10 nm. The digitized intensity of damaged regions was plotted versus wavelength. In general, all damage sites had similar spectral characteristics with varying intensity from site to site and within the same site.

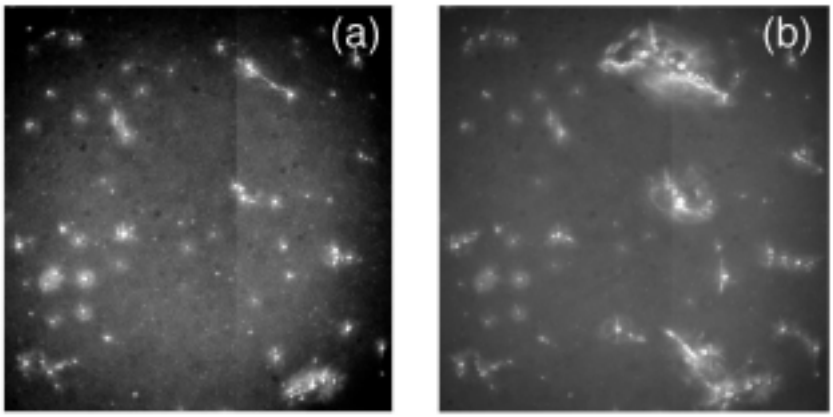



**Figure 4**: Microscopic fluorescence images of 720X620 μm$^2$ sections of the surface of three fused silica samples that were polished using different polishing processes.

Similar experiments were carried out to study the laser damaged material on the surface of DKDP crystals. This emission was used to obtain fluorescence images of surface damage site. Figs. 5a and 5b show the light scattering and emission images, respectively, of the same damage site. The emission image of this damage site, when compared to the light scattering image, revels that the emission is concentrated within the damage "crater" while areas where only mechanical damage was inflicted do not emit with equally high intensity. This behavior may be interpreted as the result of material modification due to plasma formation accompanied by high temperature, melting and a shock wave which accompany the damage process.

Surface damage is more prone to catastrophic growth, leading to damage sites that migrate to downstream optics both by inducing beam modulation and by inducing damage through surface contamination. DKDP surface damage growth appears to require a threshold fluence. Below that fluence, damage sites are stable for thousands of shots, and significantly above that fluence, they grow to centimeter size in a matter of a few shots. The modified materials is capable of absorbing a

significant amount of laser energy during exposure to subsequent pulses leading to "re-ignition" of the damage process and damaged growth. A solution to this problem may be of critical importance assuming that there will always be some damage initiators on the surface of a large optic to produce a number of damage sites. One fruitful approach may be to completely remove the absorbing material from damage sites. A preliminary effort involved solution drilling of the damaged area using a dual orifice nozzle (water injected in the center and withdrawn in a surrounding annulus). These preliminary experiments showed that this process is easy to perform, it takes only a few seconds to remove the modified layer of the sample (damage site) and it does not affect the structural integrity of the surface of the crystal.

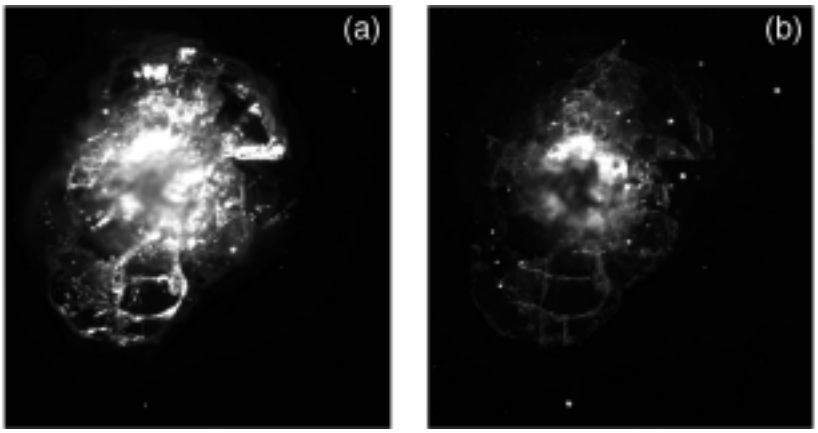



**Figure 5:** a) Light scattering and b) emission images of the same damage site on the surface of a DKDP crystal.

## 4. DISCUSSION

This work reveals the presence of defects at the damage sites by their fluorescence in the visible spectrum under UV photoexcitation. This indicates that well below the band-gap electronic excited states of these defects are excited using 355-nm irradiation giving rise to the observed emission. When a damage site is exposed to subsequent high power laser irradiation, plasma is reformed at the same site. This behavior suggests that the modified material exhibits sufficient absorption at 355-nm to start a process that is characteristic of laser induced damage. Preliminary experiments indicate that the re-ignition of plasma at damage sites takes place below the damage threshold of the undamaged material. This is a property that may be important for large aperture laser systems where damage growth is an issue that may determine the lifetime of the various optical components.

These experimental results in combination with what is generally accepted as true by the scientific community in the field of laser induced damage in optical material are suggestive of the following model for initiation and damage growth: 1) Damage initiates at sub-micron-scale sites, possibly due to polishing residue, flaws, contaminants, etc., 2) Plasma formed during initiation creates mechanical damage and optical defects in the material resulting in increased absorption, 3) Absorption by these defect populations leads to plasma re-ignition on subsequent pulses, 4) A larger plasma volume is generated causing increased production of modified material and additional defect populations, and 5) The system repeats itself at step 3 above causing even more damage, with a resultant runaway cycle, with subsequent intense laser pulses. The experiment as seen in fig. 4 shows how the process leads to chipping and cracking along with removal of material. The scattering pictures defines more of the overall observed damage that has taken place where the emission image reveals localized modified material. In order to stop the cycle leading to damage growth, damage mitigation procedures may be necessary. One of these procedures may involve complete removal of the modified material as described in the previous section.

The emission spectra arising from damage sites on the surface and in the bulk as well as from laser degraded surfaces in vacuum (shown in fig. 3) appear to have very similar spectral profiles under 351-nm photoexcitation, suggesting that the defects formed are similar (if not the same). In addition, the emission spectra shown in fig. 3 are also quite similar to the emission of preexisting defects [6] observed in KDP crystals. This may be suggestive that the defects species generated during damage are similar to bulk defect species arising from breaking of lattice bonds which are know to exist and have been studied in the past. [7,8] This may also help to devise a damage mitigation procedure or may help to better understand bulk damage issues.

## 5. CONCLUSION

Photoluminescence is observed at surface and bulk laser-induced damage sites on KDP. Results indicate the formation of a modified material at the damage sites due to intense heating, plasma formation, and rapid re-crystallization. The emission spectra from damage sites are broad with a peak centered at 550-nm. Surfaces exposed to >100 high power, 355-nm laser pulses in vacuum conditions exhibit degradation of the finishing quality associated with emission under UV photoexcitation. The emission spectra from laser-induced damage sites and laser degraded surfaces are very similar to the emission spectrum of the defect population preexisting to laser irradiation.

## ACKNOWLEDGMENTS

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