Complex morphology of laser-induced bulk damage in K$_2$H$_{2-x}$D$_x$PO$_4$ crystals

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We present a detailed study of the morphology of laser-induced bulk damage in K$_2$H$_{2-x}$D$_x$PO$_4$ crystals. We see three distinct regions of the internal damage sites: a rubble filled core, a shell that has probably been melted and compacted, and a larger outer region of slightly modified shocked material. The nature of these regions is important for understanding the impact of laser-induced damage on light scattering, which can be significant for high-power laser operation. We propose a simple model to explain the morphology and light scattering we observe. © 2006 American Institute of Physics. [DOI: 10.1063/1.2345254]

Laser-induced damage events in the bulk of optical materials have been shown to reach temperatures and pressures of over 10 000 K and 300 kbar, respectively. Despite the fact that these temperatures and pressures are more likely to be associated with a powerful underground explosion than a bulk solid state event, the damage sites in optical materials are often thought of as simple voids, occasionally accompanied by cracks. The precise nature of these damage sites is of interest because the amount of light scattered by damage sites can limit high-powered laser operation.

The present work examines the structure of laser-induced cavities in KDP and DKDP crystals. Optical scattering from the bulk damage sites is a concern because it may cause significant downstream modulation (contrast) on a propagating laser beam, even at pinpoint densities as low as a few 10’s per mm$^3$. While these damage sites tend not to grow with repeated laser irradiation, they scatter light leading to increased contrast which can enhance laser-induced damage on downstream optics. Thus, it is important to estimate the pinpoint scattering cross section and thereby estimate how many such pinpoints can be tolerated for a prescribed level of contrast.

There has been some inconsistency in reported sizes of pinpoints. Optical imaging using monochromatic (HeNe laser) illumination may lead to a larger apparent size than imaging using white light. Although no work to date has systematically studied the morphology of these damage sites, several observations in the literature depict them as voids, occasionally surrounded by cracks along the crystalline axes. Our observations show that DKDP bulk damage sites have a complicated morphology consisting of a core—empty or perhaps containing partially recrystallized material—surrounded by a shell of modified material that may be crystalline in nature. We hypothesize that this modified material is somewhat densified due to passage of the shockwave accompanying the damage initiation.

In the present work cleaving the sample though a bulk damage site gives us direct access to the modified material for micro-Raman spectroscopy and scanning electron microscopy (SEM). The damage sites are generated by exposing multiple samples of KDP and DKDP to several pulse durations (10, 3, and 1 ns, and 300 ps) and wavelengths (1064, 532, and 355 nm) with large diameter beams (1 cm). The fluence used for each set of laser conditions was selected to produce ~10 damage sites per cubic millimeter. This is enough damage so that sites may be readily found and studied while keeping the total damaged volume of the sample less than 0.1% so that individual damage sites do not interact.

We examined the bulk damage sites using SEM imaging, bright-field (transmission) microscopy, and scanning micro-Raman spectroscopy. All pinpoints had the same general form, although longer pulses and/or higher fluences tended to produce larger pinpoints. In addition, cracks appeared at higher fluence (~10 J/cm$^2$ for 355 nm, 3 ns pulses). Figure 1 shows a SEM image of a bulk damage site taken after cleaving. The plane of the break was parallel to the direction of laser propagation. We coated the exposed surfaces with ~200 Å of evaporated palladium to enhance electrical con-
ductivity and used 10 KeV electrons for the image. The inset in Fig. 1 is an enhanced bright-field microscope image of a second damage site taken prior to cleaving the crystal.

We also used a scanning micro-Raman instrument with a 532 nm excitation source to examine a third damage site. The spatial resolution of about 1 μm, was determined by the size of the probe laser beam on the sample. We scanned an area large enough to include all of the features observed in Fig. 1 (∼3200 μm²), acquiring spectra on a grid spaced by 2.6 μm horizontally and 1.8 μm vertically. Figure 2 is a false color image of the 716 cm⁻¹ wavelength intensity across this grid. The inset to Fig. 2 shows the full spectra measured at locations marked A and B in the main figure.

From the three types of measurements individual pinpoint observations in DKDP can be seen to consist of a core enclosed in a shell, both of which are surrounded by a large volume of subtly modified material with an index of refraction very close to that of the bulk material. The ∼30-μm-diam oval shown in the inset in Fig. 1 is only visible in an image with considerable enhancement. For simplicity we refer to these regions as the “core,” “shell,” and “ring,” with the designations referring to the central cavity (and rubble therein), the ∼1.5-μm-thick region immediately outside the core, and all the material outside the shell to the outer edge of the modified material, respectively. We note that the pinpoints depicted in both the SEM and transmission microscope images are different although both typical of hundreds of others.

The micro-Raman measurements show that the material outside the shell is DKDP, but that the shell itself has been modified from the bulk material. Plotting the intensity of a Raman line (found at 716 cm⁻¹) as a function of position, we see that the shell cannot consist of unmodified DKDP. The DKDP spectrum in the ring shows no indication of the material modification apparent in the shell and is only suggestive of the relatively minor modifications visible in the transmission microscope image and (to a lesser extent) the SEM image. The fluctuations in intensity within the various regions correlate to wake hackle introduced during cleaving.

Considering that cleaving the sample might also produce material modification, we requested LLNL colleagues to perform Raman measurements on DKDP under pressure in a diamond anvil cell. Under room temperature loading and then unloading to pressures of up to 3.8 GPa, the lines in the Raman spectra (observed at 716, 916 and 1180 cm⁻¹) were not seen and the spectrum returned to that of DKDP. However, when the sample was heated to temperatures on the order of 150°C under initial pressures of 2 GPa and then returned to ambient conditions, the Raman spectrum had three new lines consistent with those observed in the inset in Fig. 2.

Our results suggest that the high temperatures and pressure result in a shell of modified material surrounding the core of a bulk damage site in DKDP with a different refractive index. During the damage process, the deposited energy produces peak transient pressures and temperatures on the order of 300 kbar and 10 000 K, respectively.

Damage crater formation is similar to the problem of crater formation by an underground explosion, and a similar description can be given. To describe the material modification we assume the simplest equation of state: pressure P higher than some critical value P* results in densification to density ρ that is higher than the initial value ρ0. At the end of the laser pulse, hot ionized plasma occupies a small cavity of radius a0. There is some evidence the size of this cavity depends on the detailed history of energy deposition, but that effect is not addressed in the present paper. The pressure in the vapor causes this cavity to expand up to a final radius am. At the same time, a shock wave generated by the pressure in the cavity densifies material out to some outer radius R where the pressure has dropped just below P*. The final size of the modified zone depends on the initial radius a0, the amount of deposited energy, and the degree of densification that takes place. Assuming adiabatic expansion and invoking conservation of energy, the following relations are found to give the dependence of the radius am on the degree of compaction and deposited energy:

$$a_m = a_0 \left( \frac{d(a_0)}{2P^*} \right)^{1/5} \cdot$$
\[
\Delta n = \frac{\Delta \rho}{\rho_0} = \frac{\theta}{1 - \theta} \approx \theta,
\]

where \(\theta = 1 - \rho_0 / \rho\) as in the inset in Eq. (3). For moderate densification, the scattering cross section \(\sigma\) is given Ref. 21 by \(\sigma = k^2 R^2 G(2kR\theta)\), where \(k\) is the wave number and

\[
G(x) = 2 - 4 \frac{\sin(x)}{x} + 4 \frac{1 - \cos(x)}{x^2}.
\]

Besides wave number, the argument \(2kR\theta\) depends mostly on densification since

\[
2kR\theta = 2k a_0 \left( \frac{p_0}{P_1} \right)^{1/5} \theta^{2/3}.
\]

There are two limiting cases. If the densification is very small, the change in refractive index vanishes and there is no additional scattering from the densified region. If the densification is large, then the extent of the densified region will be small and, again, there will be little additional scattering. This means that there must be a maximum scattering cross section as a function of densification. This maximum, shown in Fig. 3, occurs in the densification range corresponding to the damage sizes observed experimentally.21

In the Fig. 1 inset one can see a relatively large ring of slightly modified material (possibly caused by the shock). From Eq. (2) we find that for the ratio of the observed ring to the core (\(\sim 10:1\)) the modification of the refractive index is smaller then 0.001. Figure 3 shows that the effect of the ring on scattering is minimal, which is consistent with the difficulty in observing this region optically.

We conclude that laser-induced bulk damage sites in DKDP exhibit a shell of modified material produced by heating and melting under pressure followed by resolidification, possibly in phase V or other solid phase of DKDP.22 This modified material is visible in optical and electron micrographs. The material in the shell has a different Raman spectrum than undamaged DKPD. It is likely that this material is densified, and has a slightly different refractive index than the undamaged material. A simple model allows the densification and effect on scattering to be estimated. This estimate predicts that scattering may be an order of magnitude larger than expected from the core size alone. Until now, bulk damage in KDP and DKDP has been thought of in terms of relatively featureless “pinpoints” consisting of small voids and/or cracks. We have found the damage sites to have a complex morphology reflecting the thermal and mechanical material response to the damaging event.

Because bulk damage sites directly cause optical scattering, estimates that bulk-site scattering can be an order of magnitude larger than that expected from the pinpoint core sizes can have significant effects on laser system design and performance.

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