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Fundamental Study of Laser-induced Surface Damage in Silica Optics

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Auspices Statement

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FY08 LDRD Final Report

Fundamental Study of Laser-induced Surface Damage in Silica Optics

LDRD Project Tracking Code: 06-ERD-035

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Abstract

The objective of this study is to develop a fundamental understanding of defect-assisted laser-induced optical absorption and its accompanying material modification in wide band-gap optical materials. A suite of sensitive high resolution optical techniques and an advanced computational modeling methodology has been developed and employed to clarify these processes in the near-surface region of fused silica. This capability will be broadly applicable to a wide class of problems involving optically-induced material modification. As a result of this project, much progress was made towards developing a fundamental understanding of defect-assisted laser-induced optical absorption and optical in silica. In particular, this work provided new insights into the dynamics of a damage event and produced the first non-destructive diagnostic with the promise of being able to predict which surface flaws in silica have high damage susceptibility.

The following publications resulted from this work: "The effect of laser pulse duration on laser-induced damage in KDP and SiO_2" [1], "The effect of lattice temperature on surface damage in fused silica optics" [2], and "Near surface metallic-like absorption and photoluminescence in wide band gap materials" [3]. The second two have been included at the end of this report:

Introduction and Motivation

Explaining the mechanisms of energy absorption from intense laser pulses to a transparent optical solid and the resulting material modifications are challenging problems of non-linear optics. Laser-induced material modification has been employed to engineer new materials such as UV-defined Bragg gratings in optical fibers [4] and Si-nanocrystals in SiO_2 formed by femto-second laser irradiation [5], but in high power optical systems, it often limits performance by damaging optics.

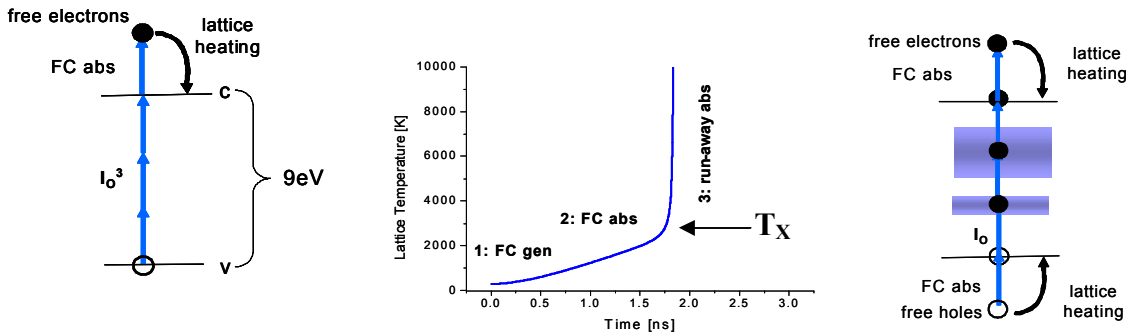
All wide band gap materials will damage at sufficiently high laser intensities through processes intrinsic to the defect-free material. Intrinsic optical damage is the result of high energy deposition through multi-photon ionization and is determined by the material's bulk electronic structure; this occurs at high intensities well beyond 200GW/cm^2. However, even the highest quality optical materials damage at fluences over an order of magnitude less than their intrinsic damage threshold and at fluences less than 10GW/cm^2. This limits the maximum operating fluence of key optical elements such as lenses, windows, prisms, and flats, including those constructed from fused silica. This extrinsic optical damage results from the absorption of sub-band-gap light by optical damage precursors (defects extrinsic to the bulk material). One of the most important optical materials, fused silica, can be made with such high quality that optical damage precursors are confined to the near surface region and are linked closely with surface flaws such as sub-surface fractures formed from polishing processes, handling scratches, and possibly surface impurities. Absorption of high fluence light by these precursors results in explosive ejection of material from the surface which leaves damage sites which are a few microns to tens of microns in diameter. Because of the importance of fused silica in optical systems, this work focuses on extrinsic surface damage in fused silica.

Energy deposition and intrinsic breakdown (damage) in the bulk of high quality optical materials [6-7] and for short pulses and high intensities [8] are relatively well understood. Unfortunately, the fundamental mechanisms behind extrinsic damage remain poorly understood due to the difficulty in identifying which defects lead to damage, the small volume occupied by these defects, and their scarcity.

Intrinsic damage (figure 1) is basically a three step process. First, free carriers (electrons and holes) are generated by multi-photon absorption of sub-band-gap photons. Multi-photon generation rates are proportional to I_0^m where I_0 is the laser intensity and (m) is number of photons involved. These free carriers (FC) absorb additional energy from the laser pulse, and subsequently lose this energy to the lattice through phonon emission. This efficient non-radiative relaxation heats the lattice during the second step to temperatures near the melting point. It can be inferred from [6] that irreversible material modification occurs when the lattice reaches temperatures near the melting point. This implies that there is an intrinsic, temperature-activated absorption, $\alpha_{IN}(\lambda,T)$, which becomes large when $T > T_X$, even for 1eV photons -- the hot silica around a precursor begins to absorb strongly. This results in a run-away absorption process which drives temperatures beyond 10,000K and produces a damage-inducing shock wave [9]. We define a temperature, T_X, which is near the melting point, to designate the temperature at which this run-away absorption begins. In the following, this model for the final stage of a damage event is referred to as the "T_X model" or the "thermally-induced run-away absorption" model.

The hypothesis here is that extrinsic damage is driven by a similar three-step process in which the initial absorption and heating to T_X can in principal be provided by defects (fig. 1c) with energy levels in the silica band-gap. Extrinsic damage occurs over the entire photon energy range from 3ω (3.5eV) down to 1ω (1eV). At the intensities where

extrinsic damage occurs, multi-photon processes with m ≥ 3 are much too inefficient to produce enough FC absorption to drive heating to the melting point. Hence, these defects must be very strong, single photon absorbers of sub-band-gap light.



(a) (b) (c)

Figure 1: Three step intrinsic damage process including the process of thermally-induced run-away absorption. (a) Energy-level diagram of multi-photon FC creation and FC absorption in SiO_2. (b) Time dependence of lattice temperature leading to damage during the three steps of a damage event. (c) Possible defect-assisted pathway for extrinsic damage.

Although the picture of figure 1 appears to fit generally, some fairly important quantitative gaps emerge when it is applied to extrinsic damage. First, there are no known silica defects which lead to efficient FC generation for $I_0 < 10$ GW/cm^2 or sufficient heating to reach T_X when exposed to known damage fluences. There is also no convincing explanation for why silica near the melting point should become suddenly much more absorbing. Measurements of the band-gap of silica at high temperatures do not show a dramatic decrease in the band-gap for temperatures up to 1600C [10].

Research Activities and Results

The main objectives of this work are to: (a) first identify a reliable experimental signature unique to the defects which absorb sub-band-gap light and lead to damage initiation and growth, and then to use this to diagnostic to help identify the physical nature and origin of these of defects; these activities focus on experiments to correlate photoluminescence (PL) signatures to damage susceptibility; (b) to use experiment and simulation to develop a consistent model to explain the dynamics of damage (fig. 1) which will help explain the effects of pulse length and multiple wavelengths on damage and the potential for damage growth; this includes methods to directly measure the rate and location of laser-induced heating in the near-surface region for fluences below the damage threshold, and models and experiments which test the hypothesis of run-away absorption.

(a) Development of a non-diagnostic for damage precursors:

Our work to identify a reliable experimental signature of damage susceptibility (a non-destructive damage diagnostic) focused on exploring photoluminescence (PL) of damage-

inducing defects, particularly their PL lifetimes. Many diagnostics have been applied to locate laser damage precursors [11-12], but no signature of damage propensity for contamination-free samples has emerged (photo-thermal detection has been demonstrated for metallic nano-particle absorbers [13]). We have developed CTP (Confocal Time-resolved Photoluminescence) imaging as a powerful diagnostic for damage precursors in silica. This methodology is motivated by the fact that optically active transitions involved in the strong absorption must also luminesce, even if weakly. Near metallic absorption suggests a very high density of electronic states typical of metals. Consequently, we look for PL which behaves more like a metal than like isolated point defects [3]. Electrons excited into continuum electronic states decay very rapidly through non-radiative, single phonon emission, so that the perceived PL lifetimes, dominated by non-radiative decy, are very short. In this work, we look for PL considerably faster than point defects (<<1ns) as an indication of a high density of absorbing electronic states. The faster the non-radiative rate, the lower the quantum yield of the emitting center and the weaker the observed PL. Because we are looking for small regions of absorbing material with weak, fast PL, we need a technique such as CTP that has the sensitivity and resolution necessary to detect very weak, localized signals as well as the ability to determine the lifetime of the luminescence transitions.

A full report of this study is attached to the end of this report in the paper entitled, "Near surface metallic-like photoluminescence and absorption in fused silica" [3]. In this work we report CTP measurements of a variety of silica surface flaws and measure their laser damage threshold with 3ns, 355nm laser pulses. In addition to point defects known to exist in bulk silica and on its surface, we identify a previously unidentified fast PL that correlates strongly to regions with a propensity for laser damage. This fast PL must be separated from slow (> 1ns) point-defect PL which can dominate the total PL signal. This is the first diagnostic with the promise of being able to predict which surface features will damage, and will be a powerful tool for understanding damage and damage resistance. CTP has helped us identify one of the most important factors limiting damage resistance in silica: a very thin (<200nm thick) defect layer associated with fractured surfaces.

(b) Experiments and simulations to probe the dynamics of a damage event

This work includes four major sub-tasks, direct high resolution measurements of non-radiative (NR) optical absorption in damage sites, ab-initio simulations of the high temperature properties of high temperature silica, experiments to test the hypothesis of thermally-induced run-away absorption (the T_X models), and simulations of the dynamics of a damage event.

Direct high resolution measurements of non-radiative optical absorption in damage sites: While the PL imaging provides signatures of damage-inducing defects, it does not directly measure the NR optical absorption which leads to lattice heating and eventually material damage. To augment these indirect measurements, we preformed direct measurements of NR absorption and heating in damage sites. Direct measurements of NR absorption are challenging but provide the most detailed view of the physics of the

damage process. In order to directly measure absorption associated with damage precursors, these measurements have been performed on laser-induced damage sites which are large enough (>300um) to easily align our measurement system to; they also have a very low damage threshold and consequently a high density of damage precursors. It has been suggested that NR absorption in a damage site occurs in a thin shell less than 10μm thick over the time scale of the pulse which is typically a few nano-seconds. The thinner or more localized the absorbing region the more difficult the local heating measurement due to time and space averaging problems. Also, NR measurements must be made with near-damage intensity pulses. Generation of a sufficient density of free carriers must occur before heating, and therefore local temperature increases may not occur until the pulse fluence is near the damage threshold.

A confocal dynamic micro-Raman microscope was designed, and Raman temperature measurements were performed to directly measure lattice temperature in a damage site for laser intensities below destructive heating. In these measurements, Raman spectra were collected during 3ns pulsed excitation. Local temperature increases in the excitation volume were directly calculated from the increase in phonon number determined by the increase in the anti-Stokes spectra relative to the Stokes spectra. The spectra were collected by a confocal optical system capable of 5μm spatial resolution. We were unable to measure any increase in the lattice temperature for fluences below the damage threshold; we measured a large black-body emission during the damage event. From this work, we conclude that precursor absorption occurs in a layer much thinner than our 5um depth resolution. This is in agreement with our CTP measurements which associate damage precursors with a thin (<200nm thick) surface layer which is especially pronounced on fracture surfaces.

We also performed single-color and two-color transmission measurements through a damage site as discussed above. Figure 2a shows the transmitted fluence of a 3ns 532nm pulse through a damage site. For fluences near the damage threshold (where the plasma emission begins), the transmission is linear. When the damage threshold is exceeded, the transmitted fluence saturates indicating that for fluences above threshold, all of the incident fluence is absorbed or reflected by the plasma. In [14], a similar saturation was reported and was attributed to non-linear absorption. Because we see essentially the same effect at much lower intensities, it seems un-likely that this is evidence of non-linear absorption prior to damage. This supports our hypothesis that precursor absorption is a single-photon absorption process.

Figure 2b shows the relative transmission of a single-color (532nm) through a damage site (transmitted fluence divided by incident fluence) over five orders of magnitude in incident fluence. These measurements detect non-linearities in absorption at fluences much below the damage threshold, but not near it.

We found that at low fluence, the relative transmission was always less than at higher fluence (within a factor of ten below where damage occurred). We interpret this as trap absorption and trap saturation – at low intensity, there is high defect absorption, but above a critical fluence, that absorption disappears as absorption channels become

blocked by saturation. We did not observe any significant non-linearity just prior to the onset of damage which could be linked to the damage event. We also performed two color pump-probe transmission experiments which behaved much like those in figures 2a and 2b. We did not detect activated FC absorption of the probe pulse by the pump-pulse.

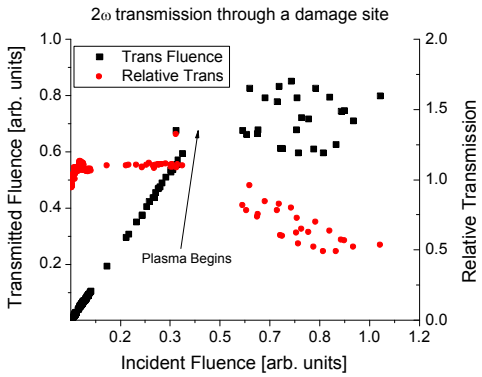


Figure 2a

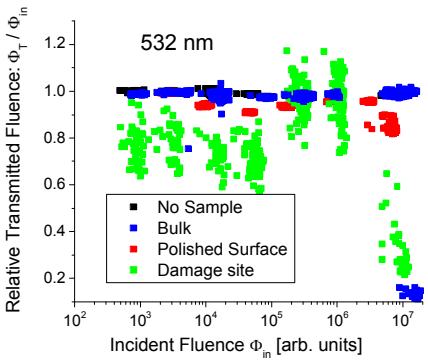


Figure 2b

Figure (2a): Transmitted 532nm fluence through a damage site showing linear transmission followed by saturation when damage occurs and a plasma is seen; (2b) Relative transmitted fluence through a damage site showing trap saturation but no strong non-linear absorber which would trigger damage.

<u>Ab-initio simulation of the optical properties of high temperature silica:</u> Ab-initio electronic structure codes were used to help identify a plausible mechanism for high temperature run-away indicated in the T_X model of figure 1. Although supported by the measurements of intrinsic damage in [6], no mechanism has been identified which would drive run-away absorption. In fact, there have been no direct low pressure measurements of the optical absorption in silica for temperatures greater than 1800K; it was shown in [10] that absorption for photon energies below 6eV was negligible at 1800K. Ab-intio techniques have improved dramatically over the last decade [15], and have shown the ability to reproduce oscillator strengths and transition energies for selected point defects (e.g., [16]). Electronic structure, wave functions and optical absorption were computed using density functional theory (DFT) augmented with hybrid functional to improve the accuracy of the excited state energies. First, we generated a "defect-free" amorphous silica structure using ab-initio DFT. Then, we performed finite temperature ab-initio band structure and optical absorption simulations in order help predict the high temperature optical properties of silica - $\alpha_{IN}(\lambda,T)$. Figure 3a shows the optical band-gap computed as a function of temperature along with measurements of the high temperature optical gap from [10]. Phonon-induced band-gap narrowing is correctly reproduced, and the hybrid-functional results show good agreement with experiment, underestimating the gap by only 1 to 1.5eV.

But, the average high temperature density of states cannot explain thermal run-away. It would take temperatures much greater than 7000K to cause the gap to close enough to have appreciable absorption at 1eV. However, we also computed optical absorption using the random-phase approximation to compute the imaginary part of the dielectric function for a large number of high temperature configurations, and found that transient absorption peaks began to occur at low energies around 2000K for our 72-atom sample; averaged over short times, these peaks form broad absorption tails into the silica band-gap (fig. 3b). These absorption tails compare well with measurements of band gap narrowing and Urbach broadening extrapolated from lower T (> 1900K) experiments [10]. This is the first ab-intio simulation of Urbach broadening; it extends our knowledge of high temperature absorption in silica far beyond measurement. The absorption predicted here is large enough to drive thermal run-away at reasonable laser fluences when T_X is greater than about 3000K providing a plausible mechanism for thermally-induced run-away. However, the measurements performed in the next section [2] suggest T_X < 3000K. More work is needed to explore whether addition processes near the surface increase the absorption shown in figure 3 providing a lower T_X. This simulation capability serves as a powerful platform to continue exploration of this effect and to help develop the physical structures linked to fast PL and the nature of damage precursors in silica and other optical materials.

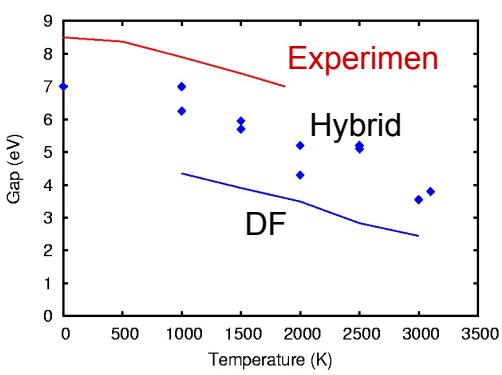


Figure 3a

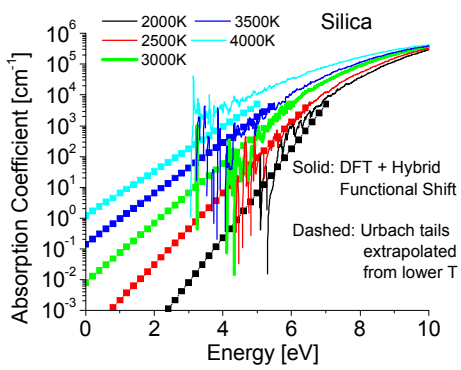


Figure 3a

Figure 3a: Average band-gap of silica computed using DFT and hybrid DFT starting with a defect-free structure; (b) simulated optical absorption including the effect of lattice vibrations at high temperatures along with Urbach tails extrapolated from lower temperature measurements [10].

<u>Testing the hypothesis of a temperature threshold for damage -- the T_X model</u>: we preformed experiments to help test the concept of run-away absorption. These results are reported in full in the attached paper entitled, "The effect of lattice temperature on surface damage in fused silica optics" [2].

According to the T_X model, the temperature of an absorber exposed to a laser pulse will increase as a function of time until it reaches T_X, at which point the surrounding material will begin to absorb and run-away absorption will drive temperatures above 10,000K,

resulting in material modification (damage). The fluence required to heat an absorber to T_X will be less in a heated sample in which the ambient lattice temperature is closer to T_X at the beginning of the damage pulse. *Therefore, the T_X model requires that the damage threshold obtained at high surface* temperature will be lower than that measured at low surface temperature. We measured the effect of temperature on the damage threshold for damage initiation for lattice temperature up to the melting point of fused silica. In order to controllably and reproducibly measure damage thresholds at these temperatures without subjecting the bulk of the sample to mechanical deformation, we heated the surface locally using a CO_2 laser. Damage tests were performed in the laser-heated spots. Our results show that at sufficiently high surface temperatures, damage thresholds are dramatically reduced. This indicates a temperature activated absorption and supports the idea of a lattice temperature threshold of surface damage. However, the temperature dependence of damage obtained here is somewhat weaker than expected based on a simple formulation of the T_X model. This work confirms the basic concept, but further experiments are required to provide a full, predictive understanding of thermally-induced run-away. In addition, we have estimated the temperature dependent absorption coefficient for intrinsic silica from these measurements.

Simulations of the dynamics of a damage event: Recent experiments show a strong correlation between the length of a laser pulse and the size of the damage site created by it; initiated damage sites sizes tend to scale with $\tau^{0.75}$, where τ is the pulse-laser length [7]. We used a model based on an intrinsic thermally-activated absorption, $\alpha_{IN}(\lambda,T)$, to determine if our view of the damage time-line was consistent with these observations of damage sites size. Our model included heat diffusion, photon transport and an Arrhenius model for high temperature absorption [2]: $\alpha_{IN}(\lambda,T) = A \exp(-T_0/T)$; the constant, A, and the activation temperature, T_0, were chosen to fit the intrinsic run-away measured in the attached paper, "The effect of lattice temperature on surface damage in fused silica optics" [2].

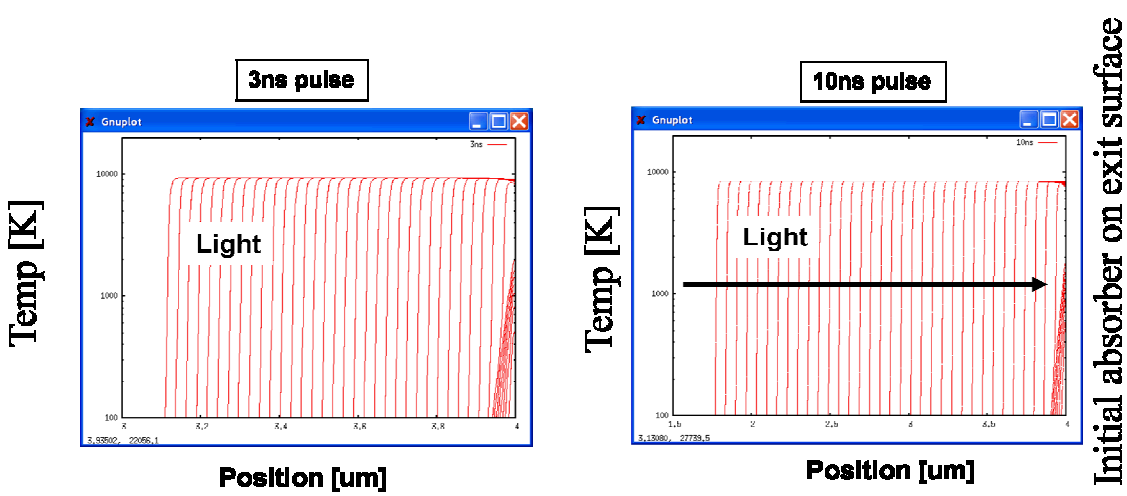


Figure 4: Simulations of temperature during a damage event using a thermally-activated intrinsic absorption model. The contours drawn at equal time-steps show the progression of the temperature profile from the initial absorption on the

exit surface of the optic back towards the laser source on the left for a 3ns second pulse (left) and a 10ns pulse (right).

These simulations were performed in one spatial dimension, and do not include many important effects, such as material motion. However, they do give a qualitative sense for the evolution of energy deposition during a damage event. This model system reproduces run-away absorption: when the temperature of the defect exceeds about 2200K, the material surrounding it begins to absorb. We found that heat diffusion drives this absorption front back toward the laser with a constant velocity (see fig. 4). This absorption front behaves like a laser-supported detonation wave, and can move much faster than a thermal diffusion current. As a result, longer pulses deposit more energy and generate deeper damage. In fact, additional simulations have shown that the maximum extent of the absorption front into the material is nearly $\tau^{0.75}$ which scales in a manner similar to the observed damage site size as a function of pulse length.

Exit Plan

This work directly addresses ignition and stockpile stewardship challenges by optimizing utilization of large ICF-class laser systems. It also serves to establish science-based rules for optics reliability prediction, provide powerful new damage diagnostics, and suggests pathways to increased damage resistance in optical materials. In particular, the CTP diagnostic is being used routinely within NIF to develop and test new optical mitigation processes. These include both local mitigation techniques such as those based on CO_2 laser processing, and global techniques (both thermal and chemical) to treat whole silica optics. Our improved understanding of the dynamics of a damage event gives physics-based support to the development of predictive rules for optics lifetime. The experimental and simulation-based tools developed are also extensively leveraged across the current optics NIF LDRD portfolio. More broadly, understanding defect-assisted absorption and material modification is a frontier problem in condensed matter physics.

Summary

As a result of this project, much progress was made towards developing a fundamental understanding of defect-assisted laser-induced optical absorption and optical in silica. In particular, this work provided new insights into the dynamics of a damage event and produced the first non-destructive diagnostic with the promise of being able to predict which surface flaws in silica have high damage susceptibility. Experiments and simulations were performed to help understand initial defect absorption and to study the dynamics of a single shot laser damage event in silica. Defect absorption was probed using direct non-radiative absorption measurements. These measurements demonstrated that initial defect absorption in laser damage sites occurs in defect layers much less than 1μm thick. We developed confocal time-resolved photo-luminescence (CTP) imaging to measure absorption indirectly. We found that regions having defects with ultra-fast (<< 1ns) photoluminescence lifetimes were strongly correlated to damage susceptibility and have begun to develop it as useful diagnostic.

We also tested the hypothesis of a lattice temperature threshold model of optical damage. This model postulates that damage occurs when the temperature of a region around an absorbing defect layer becomes higher than critical value, the surrounding material begins to absorb (run-away absorption) generating a high temperature plasma, high pressures and surface material ejection. We performed high temperature damage threshold measurements which support this model. These experiments demonstrated that damage threshold decreases with lattice temperature, and that at high enough surface temperatures, damage can occur without any defect absorption – high temperature silica absorbs strongly resulting in thermal run-away and optical damage. Ab-initio density functional theory simulations of the high temperature electronic structure and optical absorption in silica were performed which identified a possible mechanism to explain run-away absorption. This simulation platform is ideal for further studies of defect absorption in silica and other materials. Finally, we performed one dimensional simulations of a damage event driven by run-away absorption which predicted that a fast moving absorption front forms moving towards the laser source. This can qualitatively explain the pulse-length dependence of the size of laser-induced damage sites

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