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Laser Damage Precursors in Fused Silica†

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ABSTRACT

There is a longstanding, and largely unexplained, correlation between the laser damage susceptibility of optical components and both the surface quality of the optics, and the presence of near surface fractures in an optic. In the present work, a combination of acid leaching, acid etching, and confocal time resolved photoluminescence (CTP) microscopy has been used to study laser damage initiation at indentation sites. The combination of localized polishing and variations in indentation loads allows one to isolate and characterize the laser damage susceptibility of densified, plastically flowed and fractured fused silica. The present results suggest that: 1) laser damage initiation and growth are strongly correlated with fracture surfaces, while densified and plastically flowed material is relatively benign, and 2) fracture events result in the formation of an electronically defective rich surface layer which promotes energy transfer from the optical beam to the glass matrix.

Keywords: fused silica, laser damage, subsurface damage, indentation, etching

1. INTRODUCTION

The power or energy output of large lasers, such as those used for studies of inertial confinement fusion, is ultimately limited by the amount of self-induced optical damage that can be tolerated by the optical components making up the system. The issue of optical damage becomes successively more problematic as the operating wavelength of the laser moves from red to ultraviolet (UV) wavelengths. The advent of systems, such as the National Ignition Facility (NIF) and Laser Megajoule (LMJ), calls for optical components to be routinely operated at fluences that are roughly an order of magnitude higher than in previous systems.

Over the past dozen years, significant progress has been made in increasing the damage resistance of the fused silica optics operating at UV (3ω = 355 nm) wavelengths. This progress has been largely attributable to numerous technological improvements in areas including substrate quality, and grinding technology[1,2] , together with the use of improved methodologies for detecting[3], diagnosing[4] and eliminating near surface defects that can be introduced during both the grinding and polishing of optics[5]. Despite these improvements, it is useful to consider that even the highest quality fused silica optics[6, 7] typically exhibit substantial surface damage at fluences that are over an order of magnitude less than the intrinsic damage threshold of the bulk material.

While there has been a longstanding correlation[8] between the laser damage susceptibility of optical components and surface quality, the specific precursors leading to damage are not well understood. It has been suggested that the correlation between laser damage and surface quality

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is the result of fluence intensification resulting from discontinuities at crack boundaries[9] or the constructive interference between the incident beam and beams reflected from either the exit surface of the optic or from surfaces associated with surface or near surface fractures[10]. However, it is uncertain that the magnitude of such intensification is sufficient to reach the required intrinsic damage threshold of fused silica given the disparity between the band gap of fused silica (≈9 ev) and the energy of a 3ω photon[11].

An equally plausible explanation would be the presence of either an intrinsic or extrinsic sub-band gap absorber in the near surface layer of the optic. Given that the intensity of the 3ω light, which can cause near-surface damage, can be as low as a few GW/cm^2, it is likely that this absorption is a single photon event. Hence, this defect should provide strong sub-gap absorption with energy levels sufficiently close to be excited by a 3eV photon.

To date, it would appear that one such sub-band gap absorber has been identified. Specifically, several groups, including Sheehan[12] and Neauport [13], have reported strong empirical evidence that photoactive impurities, such as cerium, in the polishing layer can initiate laser damage. Such an explanation does not, however, address either the apparent correlation between surface quality and laser damage susceptibility or the subsequent growth of previously initiated laser damage sites.

In addition to chemical impurities, the near surface layer of optical components invariably contains a variety of structural, mechanical and physical defects, including densified material, plastically deformed material and fractured material. In principle, all of these material defects could contain electronic defects capable of reducing the damage threshold. Recently, confocal time-resolved photoluminescence (CTP) microscopy has identified very thin, electronically defective layers with strong sub-gap absorption on the surface of fractures of silica[14]; hence, it would appear that that fractured material is very likely another source of damage precursors. In the present study, we have attempted to determine which, if any, of these three classes of material defects are the most important in limiting the damage threshold of fused silica surfaces at fluences $<30\ J/cm^2$.

The experimental approach used to isolate potential laser damage precursors outlined above involved the following key steps:

1) The extrinsic absorption by photoactive impurities, such as cerium (III) and cerium (IV) oxides, as a competing damage mechanism was minimized through the use of a novel leaching procedure.

2) Indentation[15, 16] was used to create defects at known locations on leached fused silica surfaces. By varying the load and geometry of the indenter, it is possible to create defects that contain densified material and material that is displaced by plastic flow both in the presence and absence of fractures.

3) Localized polishing was used to remove both material displaced by plastic flow and fractured material in order to isolate densified material in the absence of both fractures and plastically displaced material.

Use of indentation is advantageous in that its inherent spatial localization allows potential precursor sites to be characterized using microscale imaging techniques both prior to and following laser damage.

2. EXPERIMENTAL / RESULTS

2.1 Materials and Methods

The substrates used in the present work were a series of 50.8 mm (2”) diameter polished fused silica windows (PW1-2025-UV) from CVI- Melles-Groit (Albuquerque, NM). All laser damage testing was conducted using focused 3 ns pulses at λ=355 nm with a $1/e^2$ diameter of 100 μm. Damage thresholds were obtained by ramping the fluence incrementally until damage occurred (R/1 damage testing). In addition to the use of optical and secondary electron microscopy, confocal time resolved photoluminescence (CTP) microscopy was used to image the defect regions induced on the surface of the fused silica substrate. The details of the photoluminescence system used in the present work have been described elsewhere[14, 17]. Briefly, the system consists of a 400 nm pulsed laser system whose output is focused onto the surface of the sample. The resultant luminescent and scattered photons are focused onto a 100 μm confocal pinhole and detected by avalanche photodiodes. The arrival time of each photon is recorded both absolutely, with a resolution of 50 nsec, and relative to the excitation pulse, with a resolution of 300 psec. A piezoelectric translation stage allows the sample to be translated in three dimensions. Studies with CTP have correlated damage susceptibility to the presence of photoactive species with fast photoluminescent decay times (τ< 5 ns); CTP has been shown to be a powerful diagnostic for damage susceptibility in silica[14].

2.2 Acid Etching and Leaching

Neauport[13] et. al. have reported a correlation between the density of laser damage initiation and the concentration of photoactive impurities in the near surface layer of fused silica optics. Similarly, Sheehan and others reported that the density of laser damage could be reduced by etching the surface of an optic with buffered oxide etch[12] (BOE), which is a combination of hydrofluoric acid (HF) and ammonium fluoride (NH_4F). As with any acidic solution containing the fluoride (F^-) or bifluoide (HF_2^-) ion, such mixtures etch (e.g. remove) the silica surface resulting in the formation of the stable hexafluorosilicate anion (SiF_6^{2-}). As the near surface layer of the silica is dissolved, impurities introduced during polishing are also removed from the surface of the optic. The removal of cerium from the near surface layer of a series of fused silica substrates etched in 20:1 BOE (Air Products, Allentown, PA.) is shown in Figure 1. In comparing the results of the samples etched 1 μm and 70 μm, it is interesting to note that the removal of more silica may not result in the removal of a proportionate amounts of cerium. This may suggest that cerium is repreciptating onto the surface of the etched substrate, perhaps as the fluoride (e.g. CeF_3 or CeF_4).

As shown in Figure 1, leaching the optic in a heated (60 °C) aqueous solution containing 40 volume% concentrated nitric acid (HNO_3), and 10 volume% concentrated hydrogen peroxide (H_2O_2) for a period of 48 hours is also an effective method of removing cerium in the near surface region of polished optics. The improvement in laser damage initiation density, when such a sample is illuminated at 15 J/cm^2, is illustrated by comparing Figures 2a and 2b.

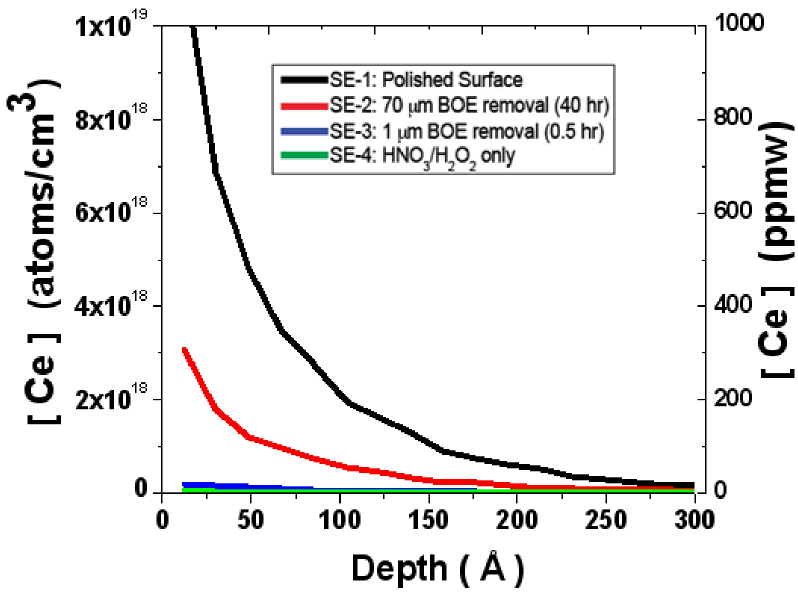
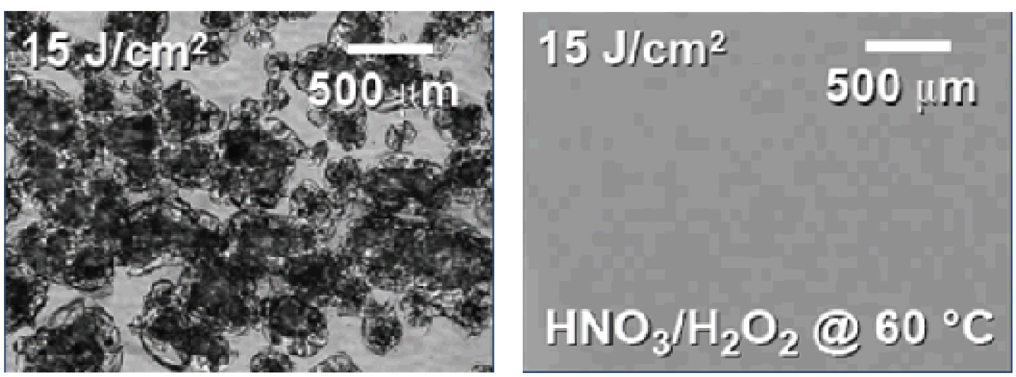


Figure 1: The concentration of Ce as a function of depth as measured by secondary ion mass spectroscopy during sputtering.



Figures 2a and 2b: Figure 2a represents a small area of a cleaned, as-received substrate exposed to 15 J/cm^2 at 355 nm (3 nsec pulse width). Figure 2b represents an area of a sample similarly irradiated after leaching with 40 volume% nitric acid/ 10 volume% hydrogen peroxide, heated to 60 °C, for a period of 48 hours.

Fluoride based etching reacts directly with the silica matrix and thus, would have a significant effect on surface morphology[4]. In contrast, the reagents used for the leaching process described here are largely inert with respect to fused silica. Thus, leaching provides an effective means of minimizing laser damage initiation resulting from photoactive impurities without modifying the silica matrix.

In the present work, all substrates except those used during the local polishing of indentations (see below) were leached in a heated (60 °C) aqueous solution containing 40 volume% concentrated nitric acid (HNO_3) and 10 volume% concentrated hydrogen peroxide for a minimum of 48 hours. In the case of the localized polishing experiment, the sample was leached following polishing.

2.3 Indentation in the Absence of Fracture

When brittle materials are subject to indentation, there are two competing responses: deformation and fracture[16]. Given a favorable indenter geometry and a sufficiently light load, it is possible to form a permanent indentation on the surface of a brittle material in the absence of fracture. Figure 3 is an SEM image of such an indentation created by applying a Knoop indenter on a pre-leached, polished fused silica substrate with a load of 0.1 N.

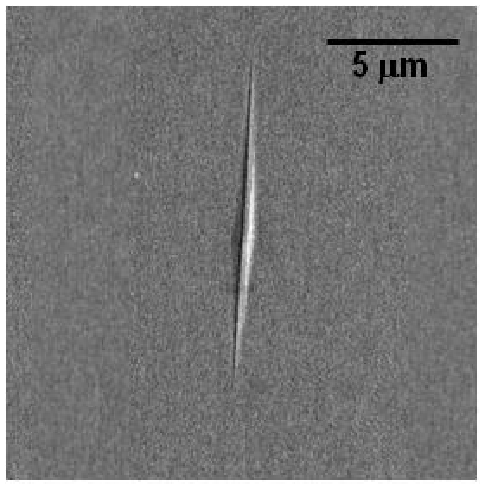


Figure 3: SEM image of 0.1 N Knoop indentation on a polished fused silica substrate. Such an indentation shows only deformation, rather than fracture.

When such an indentation is examined by confocal time resolved photoluminescence (τ <5 ns), little evidence of photo activity is seen (see Figure 4). When such indentations were subjected to localized R/1 laser damage testing, a laser damage threshold of 37 ±2 J/cm^2 was observed.

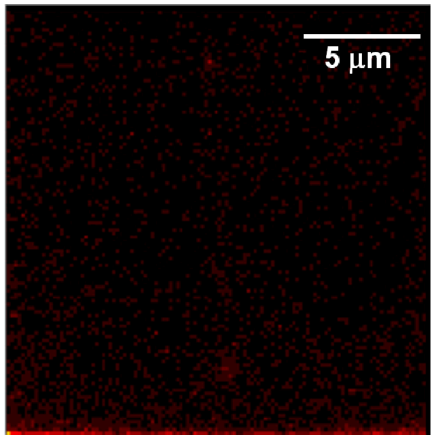


Figure 4: CTP image of fast (τ < 5 ns) photoluminescence of a 0.1 N Knoop indentation. Notice there is little evidence of photo-activity.

2.4 Indentation in the Presence of Fractures

As the load on an indenter increases, fractures will be induced on the surface of a brittle material. Near the threshold load required to induce fracture, the fractures may be quite small. For example, the width of the fractures evident in Figure 5, which were formed at the edges of a 0.5 N Vickers indentation, are typically 40-60 nm in width. Since this is much smaller than the wavelength of light, such fractures are impossible to detect by optical methods and would not be likely sources of fluence intensification.

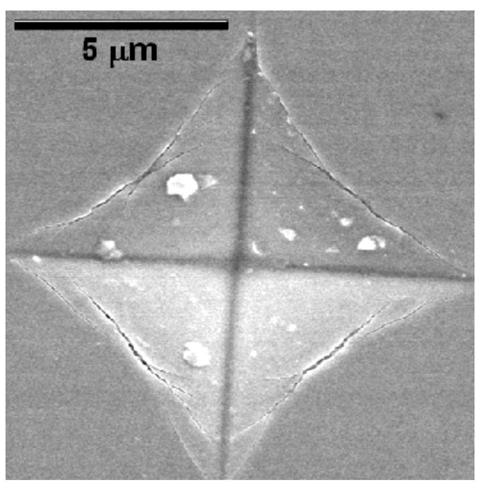


Figure 5: CTP image of fast (τ <5 ns) photoluminescence of a 0.5 N Knoop indentation. Notice there is little evidence of photo-activity.

In contrast to the CTP images of fracture free indentations, the onset of fracturing is accompanied by significant photo-activity as shown in Figure 6. When such indentations are subject to R/1 laser damage testing, one finds both a marked reduction in laser damage threshold

(7 ± 4 J/cm^2) and a coincidence between the location of fractures, the origin of the photoluminescence and the location of optical damage initiation (see Figure 7).

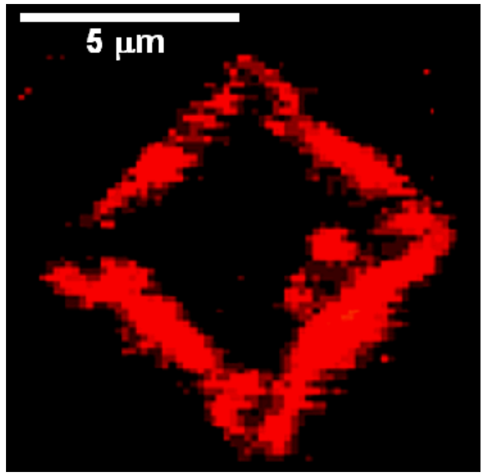


Figure 6: Typical fast (τ<5 ns) photoluminescence image of 0.5 N Vickers indentation. Note the coincidence between the location of the photoluminescence and the location of the fractures shown in Figure 5.

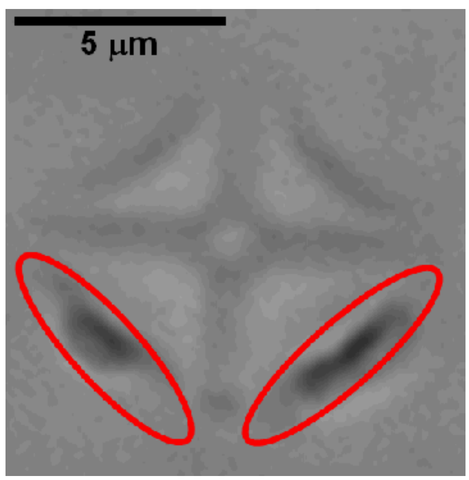


Figure 7: Optical micrograph of a 0.5 N Vickers indentation following exposure to a single 6.9 J/cm^2, 355 nm pulse of 3 nsec. Note the spatial coincidence of the narrow shear band fractures to the location of optical damage initiation.

2.5 Localized Polishing of Fractured Indentations

Permanent deformation sites, such as those shown in Figures 3 and 5, are the result of both the densification of material below the tip of the sharp contact as well as a small fraction of silica that is displaced by plastic or shear flow[18]. As shown in Figure 8, localized polishing can be used to physically isolate material that is densified during indentation from silica that is both fractured and plastically deformed. After leaching in HNO_3/H_2O_2, the photoactive behavior of the densified material was assessed by CTP (see Figure 9) and the laser damage threshold was assessed by R/1 testing and found to be 30 ±2 J/cm^2).

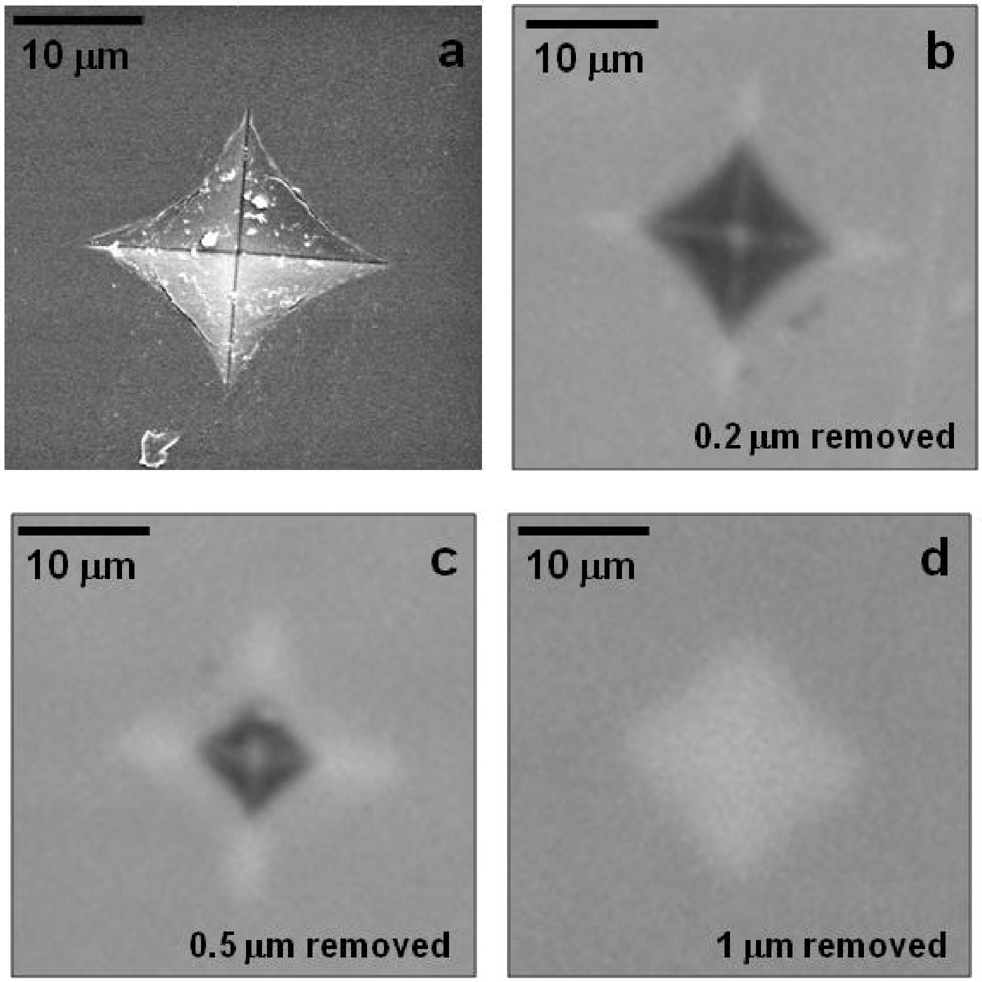


Figure 8: (a) SEM of 0.5 N Vickers indentation prior to localized polishing.
(b, c, and d) Optical micrographs of 0.5 N Vickers indentation following removal, by MRF polishing, of 0.2, 0.5, and 1 µm of fused silica, respectively

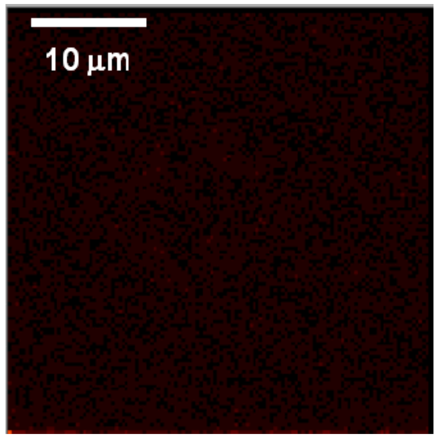


Figure 9: CTP image of 0.5 N Vickers indentation on polished fused silica substrate following removal of 1 μm of material by MRF polishing.

As was the case with the fracture free indentation, once the fracture surfaces are removed by polishing, there is little indication of photoactive behavior and there is a pronounced increase in the laser damage threshold as determined by R/1 damage testing.

2.6 BOE Etching of Indentations

The collocation of fractures, photoluminescence, and the location of laser damage initiation documented above, is consistent with a layer of material that strongly absorbs sub-band gap light. As shown in Figures 10a and 10b, removal of 150-200 nm of fused silica from the indented substrate by etching in 20:1 BOE results in a significant reduction in the photo-luminescent signal compared to the signal observed in Figure 6. Laser testing of such etched indentations indicate a laser damage threshold of 20 ±4 J/cm^2. Thus, the damage threshold of the fractured indentation can be significantly increased by removal of a small layer of defective material.

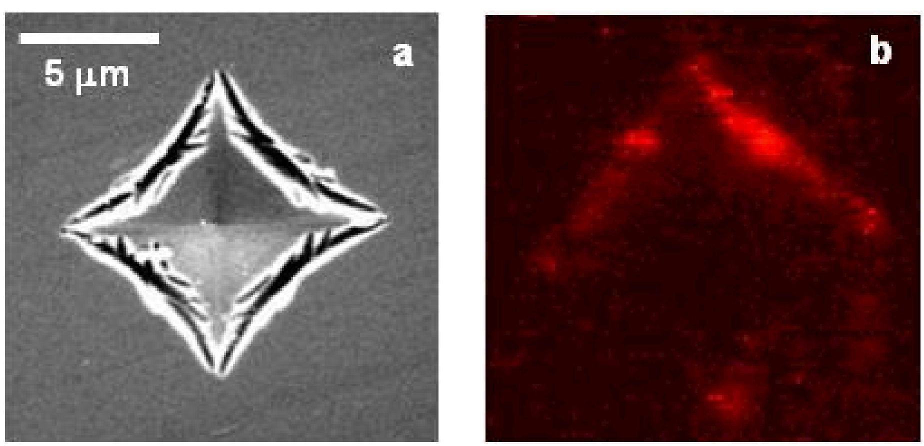


Figure 10: (a) SEM and (b) CTP images of 0.5N indentations after etching of 150-200 nm of fused silica with 20:1 buffered oxide etch

2.7 Heat Treatment of Indentations

Similarly, the photoluminescent intensity and the propensity for laser damage can both be reduced by heating indentations. Specifically, upon heating silica substrates containing 0.5 N Vickers indentations at a temperatures of 750 °C for a period of 48 hours, the laser damage threshold was found to be 37 ±4 J/cm^2. Consistent with previous observations, this increase in optical damage resistance was accompanied by a reduction in the fast photoluminescence signal (Figure 11a and 11b).

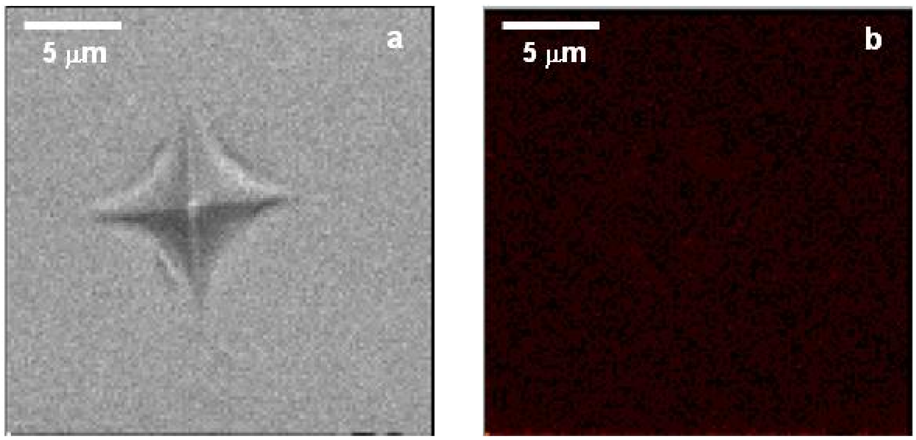


Figure 11: a) Optical and b) CTP images of 0.5N indentations following heating for 48 hours at a temperature of 750 °C

3. DISCUSSION and CONCLUSION

The present study highlights the role of two distinct classes of sub-band gap absorbers which act as precursors to laser damage on the surface of fused silica optics. The first of these are photoactive impurities that can be introduced into the near surface layer of optical components during the polishing process. Cerium compounds, particularly CeO_2 and Ce_2O_3, would be expected to be particularly important precursors given both their well known photo-activity[19] and their widespread use in the optical finishing industry[20].

Secondly, in the indentation experiments described above, we have been able to isolate the role of fracture, plastic deformation and densification with respect to sub-band absorption and laser damage at 355nm. These results show that of the three, fracture associated with indentation is dominant and limits laser damage performance. Similarly, given the dimensions of the fractures studied here and the modest changes that occur during etching and heating, there appears to be little experimental evidence that fluence intensification in the fractures plays a strong role in laser damage under the present conditions. Hence, a strongly absorbing quasi-continuum set of electronic states[14, 17] associated with the formation of fractured surfaces represents a second means by which energy can be transferred from an optical beam to the glass matrix resulting in the initiation and, presumably, the subsequent growth of laser damage. Even fractures whose dimensions are smaller than the wavelength of visible light appear to be capable of significantly degrading the laser damage performance of optical components. The increase in laser damage threshold associated with the etching and heating of indentations illustrated above is consistent with the either the removal (etching) of a thin layer of defective material or the thermally induced rearrangement of a thin electronically defective atomic surface (heating). This also suggests that it may be possible to increase the laser damage threshold or mitigate preexisting laser damage on the surface of fused silica optics using global or "whole optic" techniques[21].

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