

Resilient calcination transformed microoptics

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3D multiphoton laser lithography of hybrid resins has shown to be a viable tool for producing micro-optical functional components. The use of the calcination heat treatment also allows the transformation of such structures from initial polymer to finally glass and glass-ceramic. Although the laser-induced damage threshold (LIDT) is an important parameter in characterizing all optics, it was not known for such sol-gel-derived glass microstructures. Here we present the first pilot study regarding this parameter, wherein functional microlenses have been made, damaged and calcinated for the series-on-one protocol. The results point to the fact that the LIDT can be increased significantly, even multiple times, thus expanding the usability of such resilient micro-optics.

I. INTRODUCTION

The field of laser multi-photon lithography is rapidly progressing. More and more interesting micro-optical devices are given form at the micro-scale. Examples include conventional¹ and Fresnel micro-lenses², holographic elements³, meta-optics^{4,5} and multi-component systems⁶, most notably, micro objectives⁷. One problem overlooked with such systems is the laser-induced damage threshold (LIDT) behavior. The major limitations stem from the fact that ease of manufacturing does not guarantee a high LIDT. Arguably not all applications are demanding in this regard⁸, yet the domain of modern high-intensity pico- and femtosecond pulses might be barred.

Some attempts to measure LIDT have been made and show variation depending on: if the resin used is organic or hybrid^{9–11}, if a photo-initiator (PI) is used¹², if the structure is a thin-film¹¹, bulk object¹³ or a device^{14,15}. Technically, the way to increase LIDT is by choosing resins without PI¹⁶ and a less organic composition¹⁷. We want to go beyond this concept by using an alternative approach: making purely inorganic structures using a heat-based post-processing method called calcination, without disregarding the convenient multi-photon 3D printing method¹⁸.

Essentially, for metal-organic systems such as SZ2080^{TM19} above 1000°C²⁰, the resulting phase is an inorganic composite glass or glass-ceramic phase while retaining the printed geometry with homogeneous and repeatable shrinking²¹. Intuition dictates that transparent glassy²² structures should feature higher LIDT values and, therefore, must be more resilient to high-intensity radiation, but this idea was never tested¹⁴.

Therefore, the goal of this paper is to fabricate suspended and functional structures Fig. 1(a), in this case, microlenses, heat-treat them Fig. 1(b), and confirm the useful increase in LIDT Fig. 1(c).

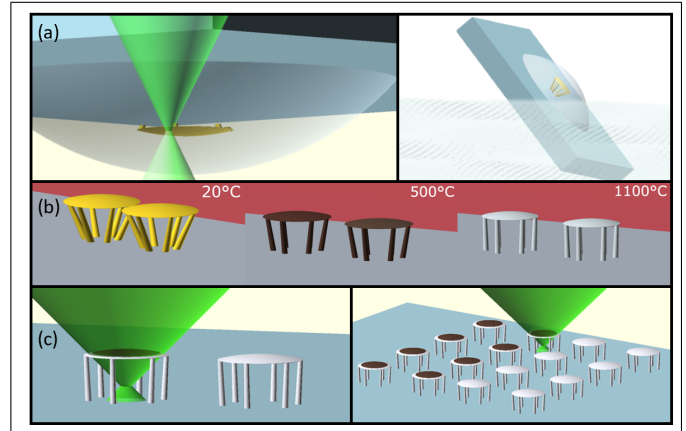


FIG. 1. The experimental principle. (a) the fabrication of the test lens structure in resin, (b) heat treatment of the structure and compliant columns, (c) the exposure of the structures to measure the LIDT values.

II. METHODS

To produce the lenses, we used the low-shrinkage organic-inorganic prepolymer SZ2080TM. The preparation and exposure and conditions (Fig. 1 (a)) were selected similarly to²³ using a 1.4NA objective, 517±10 nm wavelength and 144 fs pulse duration and a repetition rate of 76MHz. The lenses were printed on a quartz substrate. The final baseline geometry was of a plano-convex, 50 μm diameter, 300 μm focal length lens, with a thickness of approximately 2 μm. To support the lenses above the quartz substrate, pillars were printed with an inclination angle of 35° and a total height close to 30 μm. Heat treatment was performed at 1100°C with a rise time of 12 hours and held for 3h. Some reactions with the ambient atmosphere are expected, however, the final transparent phase generated at the highest treatment temperature is of the essence here (Fig. 1 (b)). Non-calcinated (NCA) and calcinated (CA) samples were qualitatively examined and exposed to the probe beam in damage tests in an array form. (Fig. 1 (c)). Qualitative characterization of their imaging function was performed in a bright-field microscope to confirm their imaging function before and after LIDT measurements. See Fig. 2 (a) for the illustrated concept. The imaging function

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was used to confirm the occurrence of significant and catastrophic damage events (2 (b)-(e)). After, they were characterized using a scanning electron microscope (SEM).

Damage tests were performed on arrays of micro-lenses. Arrays, mainly composed of 16 lenses, would be divided in half to account for damage experiments for NCA (control) and CA (test) micro-optics. Damage tests would be performed in the following sequence: an array of lenses is printed, half of the lenses are damaged before calcination, then the array is calcinated as described previously, and finally, the second half of the lenses are damaged. Laser system parameters used for all experiments were: wavelength $\lambda_1 = 1030$ nm and $\lambda_2 = 515$ nm, repetition rate $f = 200$ kHz, pulse duration $\tau = 300$ fs, Plan-Apochromat Zeiss 20x objective (0.8 NA). S-on-1 damage tests were performed with both wavelengths, exposing the lenses for 50 ms and 5 s, corresponding to 10 000-on-1 and 1 000 000-on-1 pulses.

In addition, two damage protocols are tested. The first protocol is referred to as a local-damage protocol, where the beam diameter is around $4 \mu\text{m}$ ($1/e^2$ intensity level) on the sample. The second protocol is the delocalized-damage protocol, where the probe beam is $20 \mu\text{m}$. The reasoning behind the delocalized damage protocol is to demonstrate the expected behavior where the full aperture of the lens is used.

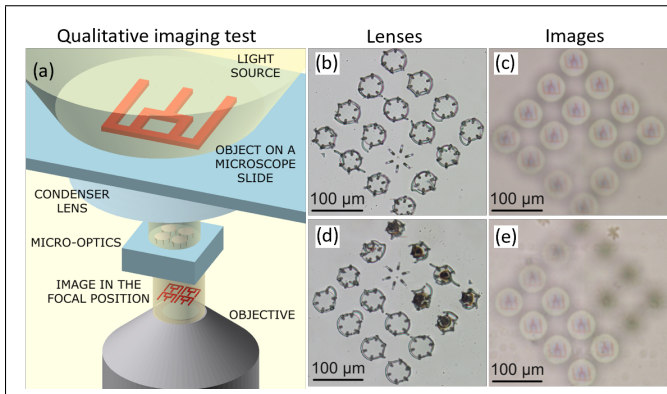


FIG. 2. Optical characterization of micro-optics using an inverted microscope: (a) image of the surface of the optic components, (b) an image of the focal position ($300 \mu\text{m}$) of the same micro-optics, (c) bright-field image after damage, (d) degradation in image quality in the focal position of damaged lenses.

III. RESULTS

A. Morphology

The observed damage morphology is shown in Fig. 2. For comparison, an example of a pristine lens is given in Fig. 2 (a). Such a lens initially is of $50 \mu\text{m}$ in diameter and, after calcination, shrinks down to $30 \mu\text{m}$. The localized damage protocol produces small damage sites. The delocalized-damage protocol produces large damage sites for NCA lenses (Fig. 2 (b)). In this case, the lenses lose their imaging function as most of the aperture becomes distorted. The damage is technically

catastrophic. On the other hand, CA lenses shown in Fig. 2 (d,e) retain their qualitative imaging function and feature small diameter ablation sites reminiscent of fs-laser surface ablation. The morphology does not differ in any meaningful manner independent of the wavelength used. The only observed difference for NCA lenses is that brown discoloration is prominent, especially for $\lambda = 1030$ nm.

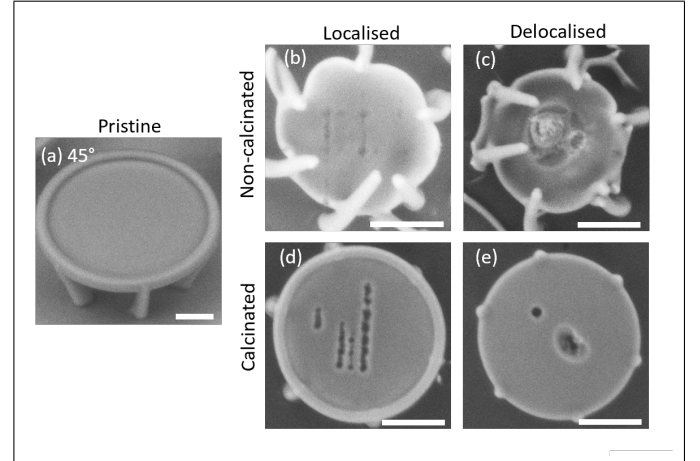


FIG. 3. SEM micrographs of micro-lenses, illustrating the typical damage morphologies observed. The scale bar is $10 \mu\text{m}$. (a) image of an NCA lens without damage, (b) local damage protocol lens damaged before CA, (c) delocalized damage protocol lens damaged before CA, (d) local protocol lens damaged after CA, (e) delocalized protocol lens damaged after CA. Tracks are formed for easier visualization of the damaged sites.

B. LIDT values

The measurement results of LIDT values are summarized in Fig. 4. We analyze a combination of cases of localized and nonlocalized damage protocols, NCA and CA, 10^4 -on-1 and 10^6 -on-1, and 515 and 1030 nm wavelengths. The NCA localized damage results correspond well in the margin of error with the ones presented in the literature: $F_{1030} = 0.57 \text{ J/cm}^2$ and $F_{515} = 0.13 \text{ J/cm}^2$.

The non-localized damage thresholds do not correspond as accurately to previous results. They are lower. However, it is essential to note that the previously known experiment in which S-on-1 damage testing protocols were employed used only up to 1000 pulse exposure, so the current results with decreased LIDT are novel.

Damage thresholds of calcinated micro-optics from locally induced damage showed the highest increase - for 1030 nm damaging wavelength, a 3-fold increase was observed from $F = 0.6 - 0.8 \text{ J/cm}^2$ to $F = 2.3 - 2.7 \text{ J/cm}^2$, using a 300 fs laser pulse duration. This damage threshold was the highest out of all measured values and contained the entire exposure duration range from 50 ms to 5 s. The highest percentile increase in resilience was observed from using a second harmonic (515 nm) - around a 6-fold increase from uncalcinated micro-optics damage tests in all exposure durations

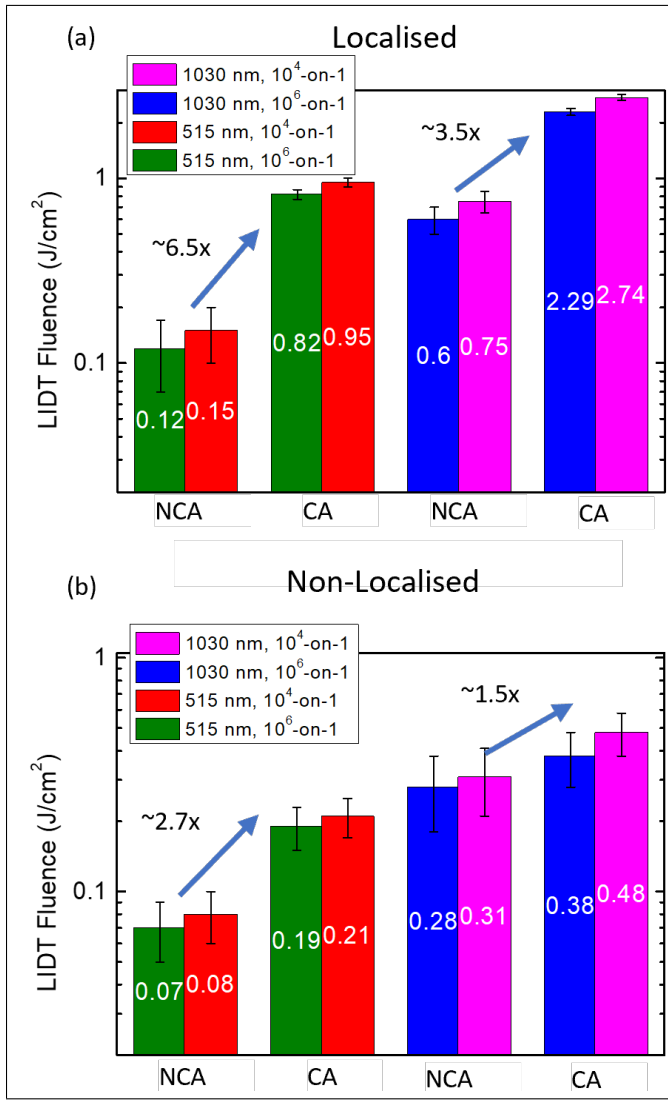


FIG. 4. Damage threshold measurement results for (a) localized damage protocol, (b) nonlocalized damage protocol.

from $F = 0.12 - 0.17 \text{ J/cm}^2$ to $F = 0.8 - 0.9 \text{ J/cm}^2$.

A decrease in damage thresholds is also observed when the laser focus position is shifted, thus increasing the exposure area on the lens compared to uncalcinated counterparts. For the 1030 nm wavelength, the most minor calcination influence was measured - damage thresholds increased only about 0.5 times from $F = 0.28 - 0.31 \text{ J/cm}^2$ for uncalcinated microoptics to $F = 0.38 - 0.47 \text{ J/cm}^2$ for calcinated lenses.

The main result observable for all cases is that the LIDT values always increase CA microlenses. The results are consistent, independent of irradiation area, testing process, etc.

IV. CONCLUSIONS

Optical damage threshold measurements of SZ2080 material after calcination have been reported for the first time. The structures have been processed at a temperature of 1100°C

and feature a significant increase in damage threshold, reaching 300-600% as a conservative estimate. This increase supercedes all measured values before^{11,12,17}. Also, the maximum measured LIDT value at $\lambda = 1030 \text{ nm}$ is $F = 2.74 \text{ J/cm}^2$. It is relatively large as it approaches the level of fused silica¹³ $F = 3.11 \text{ J/cm}^2$. This result is promising, as applications of this material in harsh environments, as postulated many times previously, are proven for optical and IR wavelengths. Thus the multiphoton lithography method combined with heat treatment can offer a technologically viable pathway to producing optical-grade glass-level performance micro-optical elements.

Finally, as this is a pilot study, more research should be done for other significant regimes, such as the nanosecond and continuous-wave damage tests. Regardless, the current results give credibility to the hypothesis that further research will also feature increased LIDT values.

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DATA AVAILABILITY STATEMENT

Data available on request from the authors

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