Article

Laser 3D Printing of Inorganic Free-Form Micro-Optics

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Abstract: A pilot study on laser 3D printing of inorganic free-form micro-optics is experimentally validated. Ultrafast laser nanolithography is employed for structuring hybrid organic-inorganic material SZ2080^{TM} followed by high-temperature calcination post-processing. The combination allows production of 3D architectures and the heat-treatment results in converting the material to inorganic substance. The produced miniature optical elements are characterized and their optical performance demonstrated. Finally, the concept is validated for manufacturing compound optical components such as stacked lenses. This is opening for new directions and applications of laser made microoptics under harsh conditions such as high intensity radiation, temperature, acidic environment, pressure variations, which include open space, astrophotonics, and remote sensing.

Keywords: laser 3D nanolithography; micro-optics; astrophotonics; 3D printing; additive manufacturing; SZ2080^{TM}; hybrid materials; inorganics; imaging; high temperature.

1. Introduction

Ultrafast laser written photonic circuits in transparent materials is a steadily growing scientific field and approaching towards practical implementations [1]. The direct write technique based on ultrashort pulses allows prototyping of dense hierarchical integrated devices of organic photopolymers [2] as well manufacturing of ultra high-performance devices made in diamond [3]. Both mentioned examples are incredible achievements individually, however a cross-road of whether choosing the CAD-CAM design freedom for a prototype or the functional materials with limited processing options is inevitable. Here we employ our developed laser additive manufacturing technique of Si/ZrO_2 tunable inorganic 3D micro-/nano-structures [4]. The approach combines a method of laser assisted precision additive manufacturing and advanced thermal post-processing solution. The laser direct writing 3D lithography enabled by non-linear light matter interaction [5] is already a well established technique for routine fabrication of diverse organic [6] and hybrid or composite materials [7]. Yet, until now, it was quite limited for direct processing of transparent inorganics of ceramic and crystalline phases [8]. On the other hand the current advances of the technique are driven vastly by the rapid progress for implementation in manufacturing of various micro-optical and nano-photonic monolith elements as well as fully assembled complex 3D components [9–13]. Thus, here we demonstrate the combination of ultrafast laser 3D nanolithography and thermal post-treatment for opening a route for production of free-form inorganic structures - specifically free-form micro-optics. Up to now it was just partially realized and restricted to limitations such as: 2D/2.5D structures [14], or millimeter-scale dimensions [15,16], or non-transparent components [17]. It is intuitively obvious and clearly anticipated that the Laser Induced Damage Threshold (LIDT) of such inorganic optical components will be of higher values preferable in practical micro-optics [18] and nano-photonic applications [19], especially taking into account high-temperature or light-intensity, chemically harsh environments,

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and heavy duty applications [20].

The aim of the work was validation of the concept, that transparent in the visible range and free-form micro-optics of inorganic materials can be made *via* straightforward combination of laser 3D printing and high-temperature calcination. The implemented workflow is graphically shown in Fig. 1.

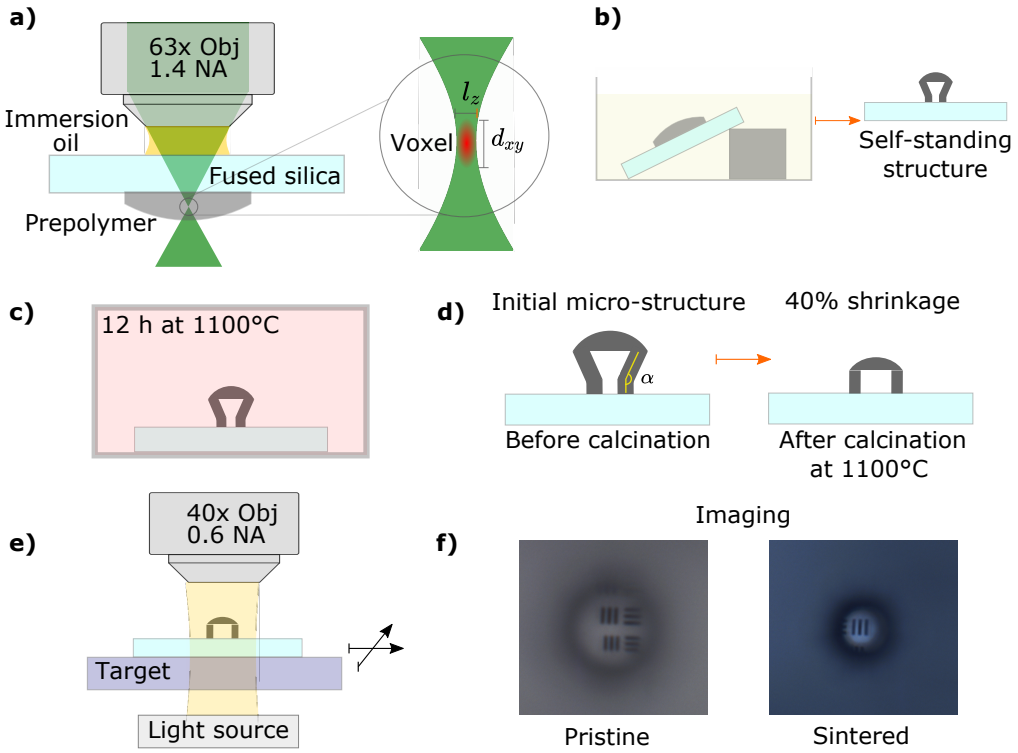

Figure 1. Schematics of the proposed approach: (a) LDW process; (b) wet chemical development bath (placing the sample with an angle results in a cleaner development process reducing the polymer waste); (c) calcination process; (d) a geometrical comparison of micro-optical structure prior and post calcination, a pre-compensation angle of the legs is shown as well as an expected shrinkage; (e) optical performance characterization of the micro-structure prior and post calcination; (f) imaging and measuring the resolving power by a calibration test target.

In order to achieve this goal a series of micro-optical components were fabricated, calcinated and characterized geometrically as their functional performance was validated. The obtained glass-ceramics 3D micro-lenses demonstrated sufficiently high optical transmittance, imaging and magnification. All together this proves it as a novel and feasible way to produce various micro-optical components with high-degree of freedom in geometry. Additionally stacking of individual elements into a compound monolith optical components was benchmarked - proving its feasibility for making custom integrated optical micro-systems. Further studies are projected towards precise evaluation of their refractive index and even potentially tuning it towards specific demands.

2. Materials and Methods

2.1. Used materials

We used the hybrid organic-inorganic material SZ2080^{TM} (IESL-FORTH, Greece) with 1 wt% concentration of Irgacure 369. A drop drying technique was used for the preparation of the sample. The sol-gel prepolymer solution was drop-casted on a fused silica substrate which is used due to its high melting temperature. A heating process on a hot plate was implemented to dry the sol-gel prepolymer drop by the following temperature stages sequence: (1) 5 minutes from room temperature to 40C leaving the sample to stay for 10

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minutes, (2) 5 minutes from previous temperature to reach 70C staying for 10 minutes and (3) 5 minutes to reach 90C from previous temperature staying for 40 minutes. By this method, the temperature gradually increases to ensure the prepolymer to acquire a uniform hard gel form to be used for the fabrication of the desired micro-optical structure. The samples were developed overnight in a chemical bath of 4-methyl-2-pentanone after the LDW fabrication process to remove non polymerized material and leaving the self-standing structures attached to the surface of the glass substrate. An optimization of the development process of the micro-structure from the flat standard is shown Figure 1 (b) with an inclination of the sample during the chemical development. The presented method for developing ensures a reduction of the polymer waste on the final sample. The sample was later left to dry at room temperature in ambient conditions prior to further examination.

2.2. Geometry

The 3D micro-structures were design to consist of two main parts: the micro-lens itself and it supports. The micro-lenses were formed by concentric circles which allowed a high control over the fabrication parameter, i.e, the fabrication light intensity at the center of the lens to avoid burning and defects as shown in Fig. 2 (a). We designed a 50 μm of diameter micro-lens with 65 μm radius and 5 μm height where such characteristics are shown in Fig. 2 (b). Three different arbitrary selected compensation angle were implemented in the support of the micro-lenses: 0, 16 and 26. The Figure 2 (c) shows a preliminary view of the design of micro-lenses and the difference in the supports' angle chosen to precompensate the bending of the supports due to a expected down to 70% shrinkage (reduction by a factor of ≈ 1.4) of the micro-structure after the calcination process.

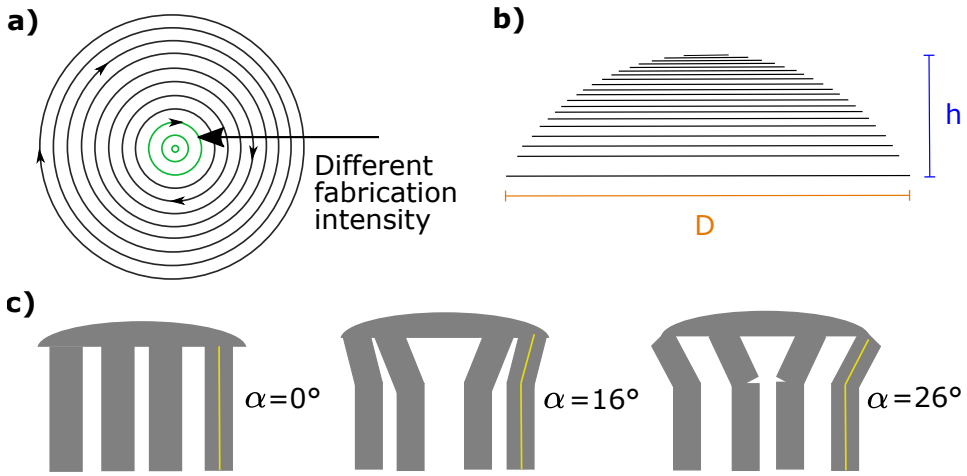

Figure 2. Fabrication strategy characteristics: (a) Top view of micro-lens fabricated by concentric circles with tunable intensity (within central part of the scanning a 10% decrease of nominal value was applied); (b) schematic of micro-lens design parameters; (c) micro-structure design: pre-compensation angle α of micro-lenses' supports.

2.3. Employed equipment

The principle employed laser fabrication equipment and the production procedure sequentially was described in details previously [21]. The micro-lenses were fabricated by 3D LDW by photo-exposing the prepolymer using the second harmonic femtosecond beam (λ centered at 515 nm) of a Yb:KGW laser with a pulse duration of 300 fs and repetition rate of 200 kHz. The beam was focused into the prepolymer drop by a Zeiss 63x 1.4 NA microscope objective under the oil immersion method with Immersol 518 F as shown in Figure 1 (a). The fabrication intensity was in the order of 0.23 TW/cm^2 with an around of 10% reduction of the intensity at the center of the micro-lens to avoid burning and defects.

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2.4. Calcination

In order to convert the laser 3D fabricated organic-inorganic micro-optics the calcination process was applied: a heat-treatment at performed at 1100^{o}C to remove the organic components as was applied for diverse architectures [4,8]. The calcination process was performed in a high temperature Nabertherm oven, raising the temperature for 12 hours until reaching 1100^{o}C and keeping it for 3 hours. A cooling curve was designed to slowly decrease the heating of the sample, from 1100^{o}C to room temperature. Though in principle all photopolymers will experience shrinkage while sintering, just hybrid ones enable conversion into inorganic substance phases. In comparison, the SZ2080^{TM} hybrid was shown superior for quality structure production in respect to OrmoComp® [22].

2.5. Optical and scanning electron microscopy characterization

The initial characterization was done by optical microscope (OM) to confirm the survival from the development of the micro-objects. Then the physical dimensions and the surface quality of the micro-optical structures were performed using a Scanning Electron Microscope(SEM, Hitachi TM-1000 and Thermo Scientific Quanta 250) where no metallic coating was applied.

2.6. Performance evaluation

The optical performance was obtained judging the resolving power of the micro-lenses before and after the calcination process using the optical microscope for imaging purposes. A target unit Thorlabs R3L1S4P - Positive 1951 USAF provided the resolution lines to obtain the corresponding resolving power of the micro-lenses. The micro-lenses were placed directly over the target unit and manually aligned to different lines groups to perform their imaging using the transmission mode of the optical microscope (illuminating with bright field white light). By translating the cover-slip where the micro-structure were standing as shown in Figure 1 (e), it is possible to image the group lines from the target unit and obtain the resolving power of the micro-lenses in both stages of the experiment as presented in Figure 1 (f): prior and post calcination to compare any change in their optical performance.

3. Results

We have used light intensity at the sample as the key irradiation parameter determining the non-reversable light-matter interaction, since the photomodification occurs only when and where a certain light intensity level is reached. The Intensity - (I), which takes into account the measured average laser optical power – P, optical systems' including objective transmittance – T, pulse repetition rate – R, and single pulse duration – τ . is can be expressed the following:

$$I = \frac{2PT}{Rw_0^2\pi\tau}. \quad (1)$$

More specifics and details regarding laser exposure parameters including polymerization and optical damage intensity threshold behaviour can be found in the recent review topic covering spatio-temporally confined light and its initiated physical-chemical polymerization mechanisms [5]. Based on this sole parameter the light processing conditions can be significantly easier reproduced while employing various pulsed laser sources with different average powers, pulse durations, repetition rates and energies, exposure doses and durations.

The microstructures were fabricated using a concentric circle scanning method with intensity of 0.23 TW/cm^2. This scanning method presents the advantage of high control of the fabrication parameters allowing to reduce 10% of the intensity at the center which proved to avoid burning at the center of the micro-lens and defects which affect their

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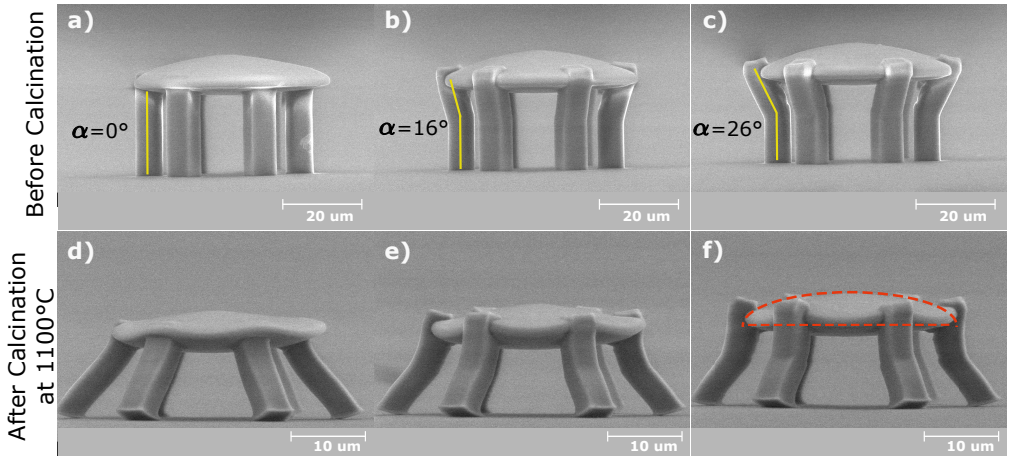

Figure 3. Shrinkage and shape precompensation of calcinated microoptics- First row shows the initial shape of micro-lenses of 50 μm diameter prior calcination with support's angle of a) 0° , b) 16° and c) 26° . Bottom row d) - f) show the same microstructures after calcination at 1100^{0}C. In f) arrows indicates the preserved shape of the lens despite the overall structure, mainly the legs, being partially distorted. Yet the central part of the volume is still lens like and thus performs as micro-optical component (demonstrated in Fig. 4).

optical performance. The SEM images prior calcination in the upper row of Figure 3 shows the three different arbitrary angles that were chosen to study as precompensation supports' angles.

The obtained resolving power of the calcinated microlenses was determined to be 4.39 μm (line size) or 228 lp/mm based on line group 7 item 6 in positive 1951 USAF target as shown in Fig. 4.

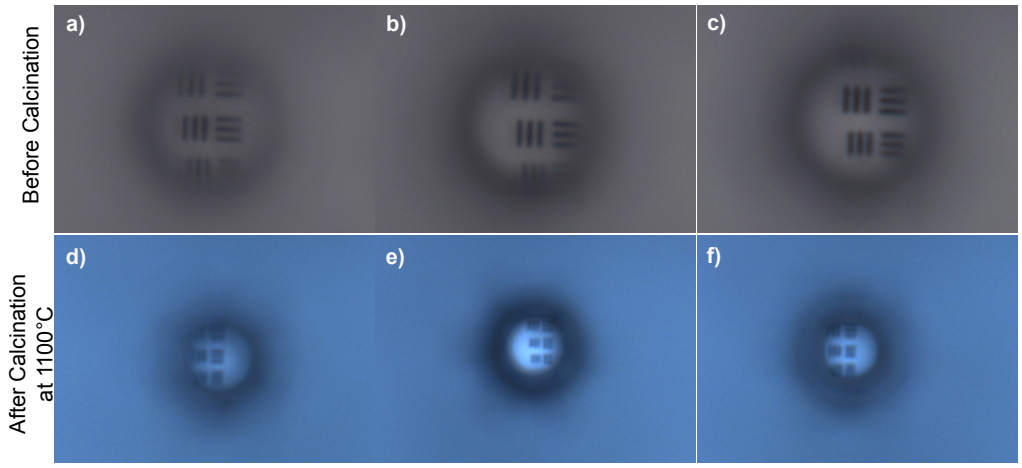

Figure 4. Optical performance of the produced microlenses. The top row shows the imaging of a target prior calcination while bottom row shows the imaging after calcination. All lenses presented a resolving power of 4.39 m (228 lp/mm group 7 item 6 in the 1951 USAF target).

The dimensions of the fabricated micro-structures were retrieved by two different methods. The diameter (D) of the thin spherical micro-lenses was obtained by an analysis of top view of images taken by optical microscope in transmission mode and compared with the side view of SEM images of the structures, both analysed using ImageJ software. The Table 1 shows the comparison on size for optical microscope and SEM images prior and post calcination process. The diameter of the micro-lenses shows the repeatability of

Micro-structure	Before	After	Shrinkage	Focal Distance
Supports at 0^o	49.3 μm	28.6 μm	42%	40.4 μm
Supports at 16^o	49.0 μm	28.8 μm	41.3%	38.0 μm
Supports at 26^o	48.5 μm	28.5 μm	41.3%	37.7 μm
Average	48.955 $\pm$ 0.5 μm	28.6 $\pm$ 0.5 μm	42.7 $\pm$ 1.5%	38.7 $\pm$ 1.7 μm

Table 1: The micro-lenses geometrical and focussing characteristics. The micro-structures were fabricated with same dimensions over three different supports structures, measured using SEM before and after calcination. The values of diameters were retrieved by a side view of the micro-lenses as shown in 3 and the focal distance was measured as visualised in 1. The shrinkage ratio and averaged values were calculated accordingly.

the fabrication with results of 50 $\pm$ 1.5 μm. The results after calcination at 1100^{o}C shows the shrinkage of the structures by around 40%.

Within the limitation of the employed techniques and equipment in the current study we could not obtain the precise shape of the lenses and measure the exact focal distance in order to estimate the refractive index (n). However, due to densification of the material during calcination it is expected to increase as it was observed for glass preparation out of ZrO_2-SiO_2 sol-gels. Namely for the SZ2080^{TM} like material it can be up to n = 1.617 [23].

4. Discussion

The LDW 3D nanolithography enables exposure dose dependent modification depth (degree of conversion / polymerization degree) which can offer 4D option in tuning the n and at the same time requires even more precise adjustment of laser processing parameters as geometry is not fully compliant with optical density [24,25]. It was reported that thermal post-curing can serve add an efficient strategy eliminating the process parameters sensitivity in the mechanical properties of two-photon polymerized materials [26]. So here we see the proposed calcination route as the way to exclude the n variation of the micro-optics ad the conversion to inorganic substance after evaporation of organic substances leaves no memory effect of exposure. This is a very important issue being recognized in free-form 3D microoptics. Furthermore it allows extinction of any photo-initiator used during the laser photopolymerization, as an organic molecule which is non-preferable due to its absorbance [27] and yellowing effects [28] - both limiting optical performance of microoptics.

In regard to Space applications it is a rising interest in both technological light-based solutions (e.g., materials providing resistance to ionization radiations, Space-grade optical fibers, etc.) and in light-driven natural phenomena that could be exploited especially for outer space applications (e.g., Solar sails). We anticipate the reported findings to be valuable for advancing this direction forward.

Finally, we produced benchmarking structures resembling micro-optical components as free-standing, mounted and assembled miniature systems, shown in Fig. 5 (a-c) respectively. As the geometry of the manufactured pristine element can be arranged freely to pre-compensate the calcination induced sintering it can be simple adjusted for any architecture by including the angle α in respect to non shrinking surface of the substrate.

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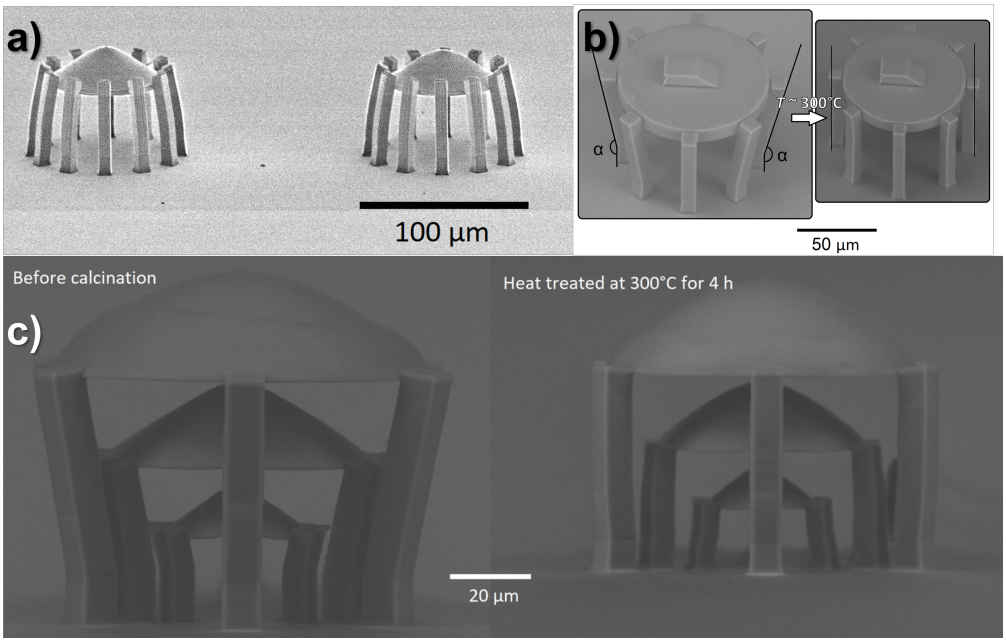

Figure 5. Scanning electron micrographs of a few benchmarking micro-optical components validating the feasibility of the proposed methods for the manufacturing of assembled devices: a) - suspended free-standing aspheric microlenses; b) - microprism on a pjedestal with pre-compensated angle α for calcination; c) - 3 stacked microlenses before and after hear treatment. All of the examples prove the final free-form geometries are achievable via shrinkage dimensional pre-compensation in pristine material and perfectly arranged architectures after sintering.

It is worth noting that the developed approach is in principle compatible with applying bio-derived plant-derived resins as organic ingredients of the hybrid photopolymer prior to the calcination, thus evapourating the renewable resources based instead of fossil originating synthetic polymers [29]. Also, the proposed route is compatible with the multi-scaling options within various existing and emerging platforms [30].

5. Conclusions

The performed conceptual work was experimentally validated as glassy 3D microlenses were made, their transparency, imaging properties were approved, and the achieved resolving power reached 4.39 μm. In overall, it can be summarized to the following conclusions:

1. Laser multi-photon 3D nanolithography of hybrid materials in combination with high temperature calcination is enabling additive manufacturing of free-form micro-optics out of transparent and pure inorganic glasses.
2. The proposed method offers advantage of uniforming the material in respect laser lithography 3D structuring and developing process, thus making the n insensitive to the specific exposure conditions by improving its internal homogeneity and surface quality [31].
3. The future work will be targeted for improving the element itself by additionally precompensating the lens shape (it can be made concave initially to balance the volume of the material), optimise calcination treatments (taking into account the specific elevation / cooling steps), modifying the pristine material (some different Si:Zr ratios as well as validating other inorganic ingredients).
4. We anticipate it as an strategy extending the additive manufacturing of inorganic 3D structures offering high complexity integrated devices for micro-sensing [32], nano-fluidic [33] and astro-photonic [34] applications.

5. Finally, the developed methodology is offering production of highly resilient 3D micro-optical components for harsh chemical, mechanical, pressure and temperature variation environments, including high optical damage threshold.

This pioneering work is opening new dimension for true 3D and free-form inorganic micro-optics and extending the possibilities of well established laser multi-photon 3D lithography as mature LDW technology.

Author Contributions: D.L.G.H. and S.V. - experimental modelling, fabrication, calcination, validation and characterization, preparation of manuscript and figures, G.M. - calcination experiments, A.C. - construction of optical experimental schemes and provision of resources, D.G. - supervision of experiments and investigation methodology, S.S. - consultation and data curation regarding calcination, S.J. - formal analysis and interpretation of the results, drafting, review and editing, M.M. - conceptualization, project supervision, funding acquisition, drafting, review and editing. All authors have read and agreed to the published version of the manuscript.

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Conflicts of Interest: The Authors declare no conflict of interest.

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