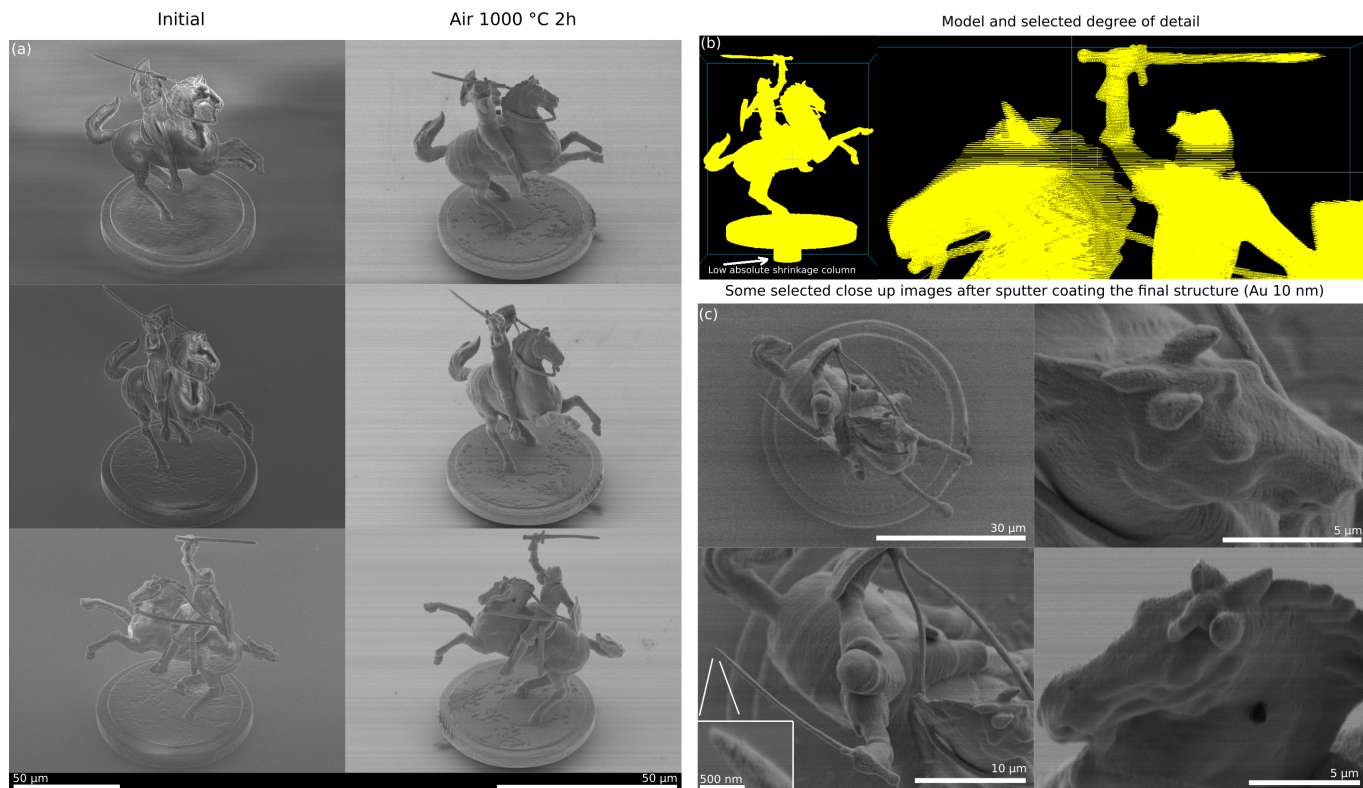


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Additive-Manufacturing of 3D Glass-Ceramics down to Nanoscale Resolution[†]

Darius Gailevičius,^{*a,b} Viktorija Padolskytė,^a Lina Mikoliūnaitė,^{c‡} Simas Šakirzanovas,^{c‡} Saulius Juodkazis,^{*d,e‡} and Mangirdas Malinauskas^{*a}



S. Fig. 1 Uniform 3D down-scaling by sintering. (a) SEM micro-graph of a glassy micro-sculpture after heating at 1000°C for two hours (right). Initial dimensions were 1.7^x larger; note the different scale bars. (b) A non-isometric visualization of the computer-aided-design (CAD) model used. (c) Close up view images of a heat treated structure after sputter coating.

^a Laser Research Center at Vilnius University, Sauletekio Ave. 10, Vilnius, LT-10223, Lithuania; E-mail: darius.gailevicius@ff.vu.lt; mangirdas.malinauskas@ff.vu.lt

^b Femtika Ltd., Sauletekio Ave. 15, Vilnius, LT-10224, Lithuania

^c Faculty of Chemistry and Geosciences, Vilnius University, Naugarduko Str. 24, Vilnius, LT-03225, Lithuania; E-mail: simas.sakirzanovas@chf.vu.lt

^d Swinburne University of Technology, John St., Hawthorn 3122 Vic, Australia; E-mail: sjuodkazis@swin.edu.au

^e Melbourne Centre for Nanofabrication, the Victorian Node of the Australian National Fabrication Facility, 151 Wellington Rd., Clayton 3168 Vic, Australia

1 Preparation of SZ2080 powder

The pulverized samples for XRD were prepared by a different method than the structures that were nano/micro-direct laser structured since a comparably large (macroscopic) amount of material was required. Here we specify the used procedures since they were less common.

While the pre-polymer is usually prepared by starting with the condensation reaction of the metallo-organic part by heating to temperature no more than 100 °C for a few hours, the powder sol-gel precursor for analysis had to be made as a dry sample. Therefore, heating for 70 °C for 72 hours was performed. It was confirmed that the sample had not been polymerized by its dissolution when immersed in the pure iso-butyl-ketone developer for one hour.

The dried resist was ground up to a fine powder and exposed using the fourth harmonic of an Nd:YAG laser. The parameters were as follows: wavelength was $\lambda = 266$ nm, pulse duration $\tau \approx 5$ ns, pulse energy $E_{imp} \approx 25$ mJ, pulse repetition rate $f = 2$ Hz, the beam intensity profile was a flat-top with diameter of ~ 1 inch. The powder was laser exposed for 6 hours while being mechanically mixed; the dry amount of powder was approximately 300 mg. The mixture was developed in a 2-propanol bath while being agitated for 48 hours. After filtering out the solid polymer particles, we confirmed that polymerization had occurred by observing that it was not dissolved in iso-butyl-ketone when immersed for 1 hour.

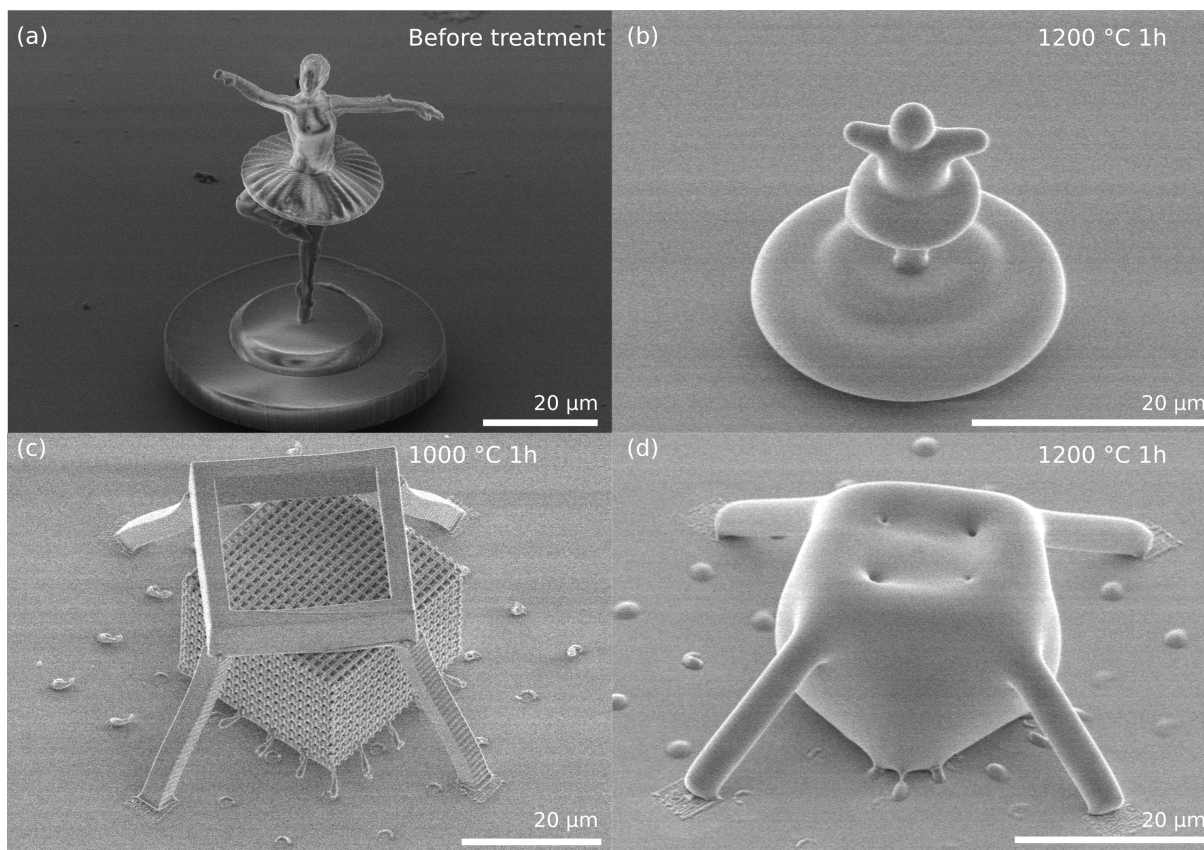
After drying the powder at room conditions for 7 days, heat-treatment was performed at the indicated temperatures in corundum crucibles.

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2 Geometric changes accompanying formation of the ceramic phase

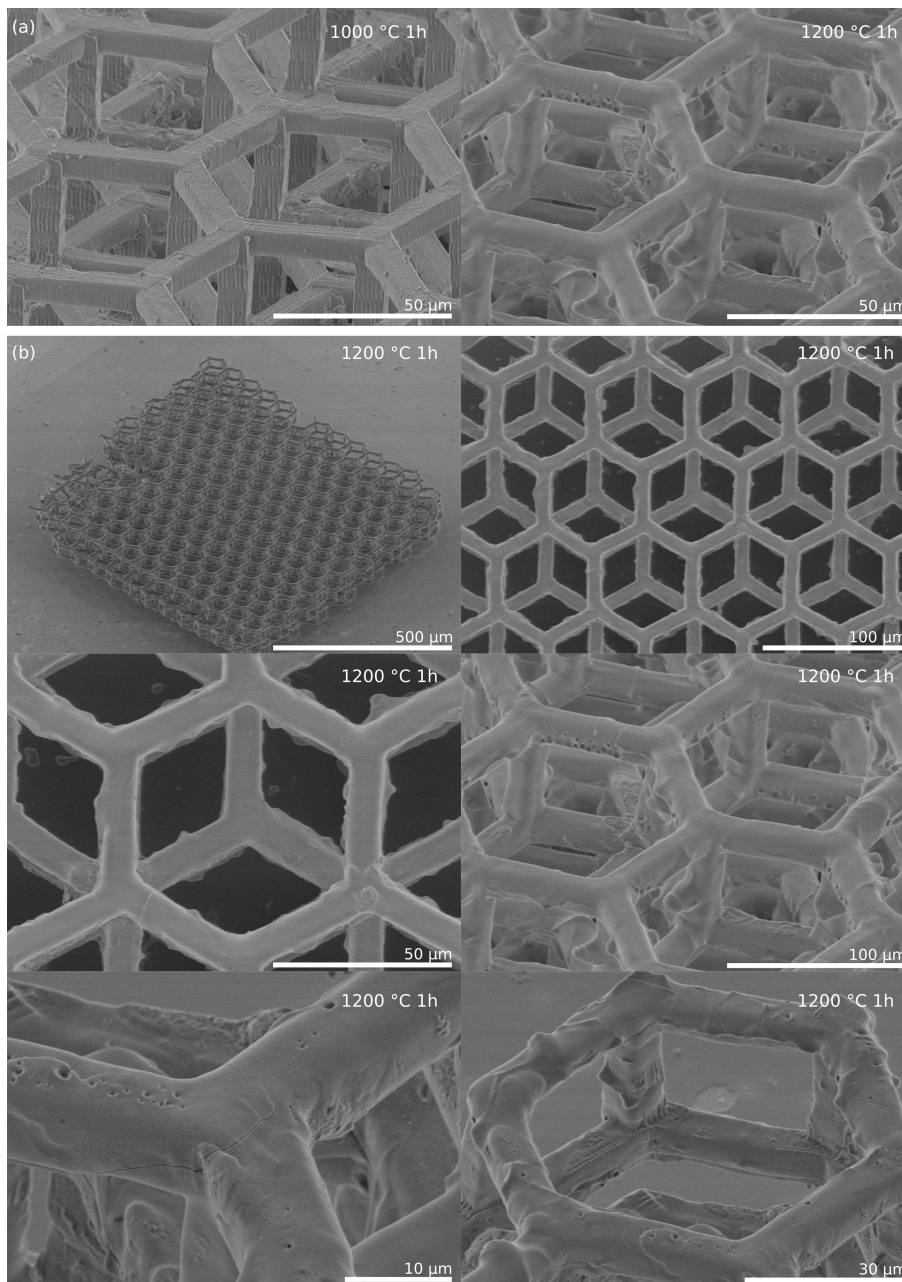
Here we discuss transformation of geometry of the structure during transformation to the ceramic state as the temperature is increased. Strongest changes occur after the threshold of $1100^\circ\text{C} < T$.

A short qualitative analysis of geometrical changes for a selected treatment temperature of $T = 1200^\circ\text{C}$ follows next. For small



S. Fig. 2 SEM micrographs of a fine-feature ballerina dancer (free-form) sculpture*: untreated (a) and thermally annealed ceramic structure (b). Also, a periodic 3D grating with a cage is shown in a glassy (c) and ceramic (d) phase.

*For reproducibility purposes we note that the STL model used here is publicly available and was retrieved from <https://www.thingiverse.com> on September 20, 2017 under the name "Ballet Dancer 03" as published on October 11, 2016.



S. Fig. 3 SEM micrographs of large area scaffolds after heat treatment at different magnifications; temperature and duration of annealing are indicated on SEM images.

samples of free-form structures and 3D lattices, the results are shown in S.Fig. 2. Structural elements having a diameter less than 3-5 μm succumb to melting or at least softening followed by surface tension induced deformation (rounding). This can be advantageous for indirect morphing into new shapes with improved surface smoothness^{1,2}.

For structures with larger features, such as scaffolds examined in this study, the geometry is maintained as shown in S.Fig. 3. The S.Fig. 3(a) shows that small topological features such as textures on the vertical columns present in the initial glass-phase structures disappeared in the ceramic state. Also, the right angles horizontal beams become rounded. However, the pattern structure was maintained after heat treatment as shown in the SEM micro-graphs S.Fig. 3. Some random cracks can be observed in the annealed structures, however, since the structures were not attached to the substrate and had to be handled multiple times when transferring them mechanically from substrate to substrate (glass substrate - fabrication, corundum substrate - furnace, adhesive carbon tape - SEM imaging) we cannot exclude the cause of cracks being due to a mechanical strain from handling.

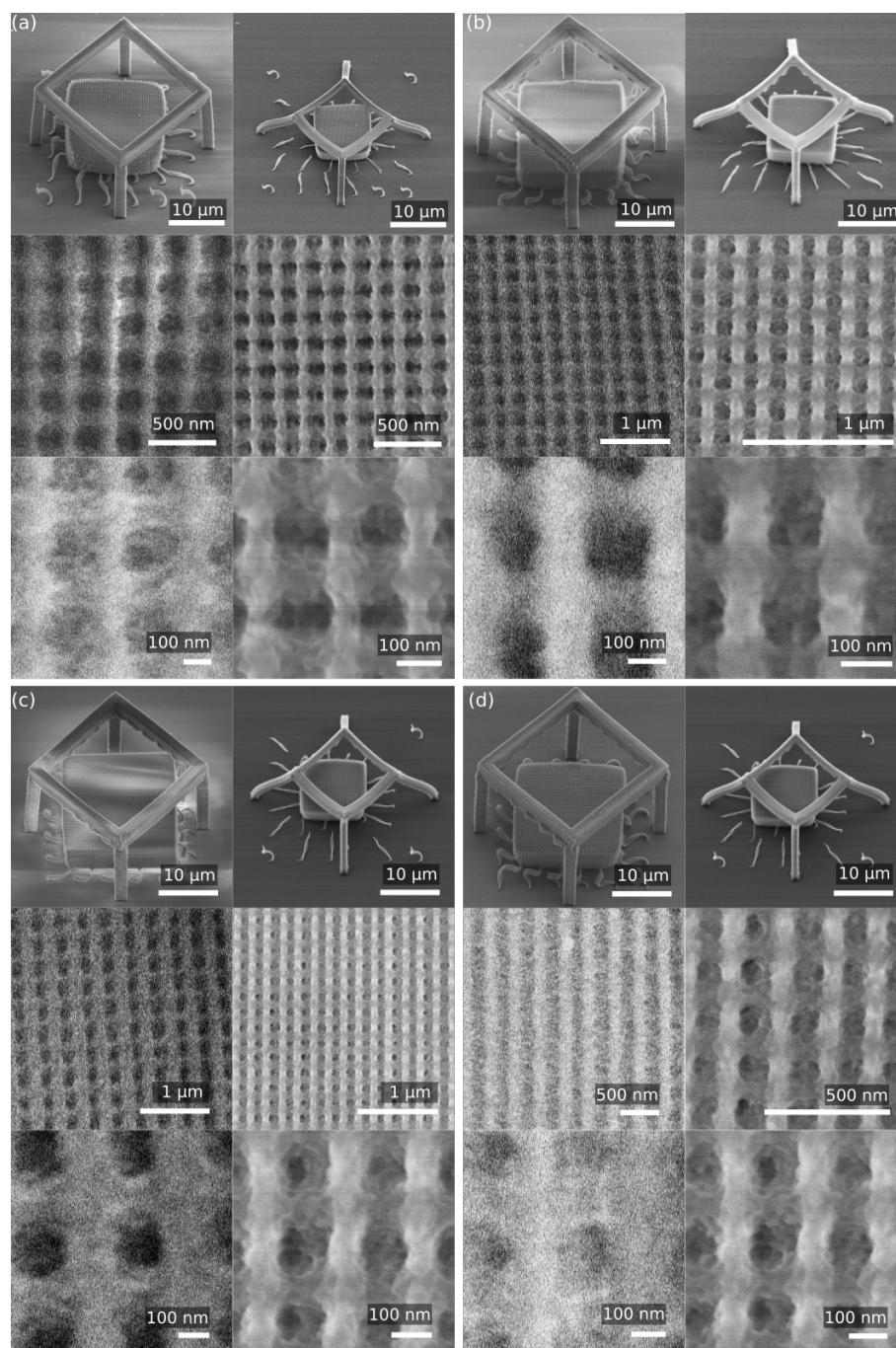
We summarize that for the particular case of the DLW structures having feature sizes smaller than 3 μm , they are strongly affected by the thermal re-flow process, but the structures with features larger than approximately 10 μm rescaled by maintaining the original outline shape.

3 High resolution structures

Here we present additional images of the structure shown in the main text Fig. 4(d) in S.Fig. 4 and demonstration of achievable nanoscale resolution. All structures have been fabricated at the same exposure conditions on thin sapphire pads and heat treated at 1000 °C for 2 hours. We note that the structures have been produced at the bottom of the fabrication window. This means that the cross-linking degree is qualitatively minimal and about 50% of attempts resulted in a standing structure with inevitable shrinking (from initial 25 to $\sim 18 \mu\text{m}$) even before heat treatment. Such probabilistic behavior is normal in stereo-lithography, yet means that each structure is, at least, slightly different.

For this reason we had to examine the structures before and after heat treatment without reference to fixed control samples. During examination with the SEM (Hitachi SU-70) we used low (2 kV) acceleration voltage to avoid electrostatic force or/and heat damage to our samples to which they are prone. Also, we had to skip a standard conductive layer deposition protocol, because the dynamics of layer deposition is not exactly predictable on samples of different porosity. This resulted in a lower contrast images of the initial structures compared to the final structures.

The heat treated structures have been imaged with a higher imaging resolution, due to the fact that the final structure is inorganic: less organic and more resilient to heat damage. Those samples are examined with higher acceleration voltage (10 kV) without damaging the structure and allows to more clearly resolve the typical top layer morphology.



S. Fig. 4 SEM micrographs of fine-feathered photonic crystal structures. (a) Structure is the one from the main text Fig. 4(d). (b,c,d) Typical features observed for different samples. For each case, the left correspond to the initial structure and the right one to the heat treated structure.

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