

# Glass-ceramic crystalline 3D micro-/nano-structures: preparation to application

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Undoubtedly, ceramics and ceramic-like materials cover an important part in science and industry, because it can withstand immense thermal, mechanical, chemical and other hazards. Making use of these properties at the micro- or even nano-scale is a topic of increasing interest. While 3D ceramic structures can be made in a multitude of ways, ceramic materials in question might be difficult to process subtractively on the microscale. A practical approach is to use additive 3D direct laser writing in hybrid organic-inorganic prepolymers with subsequent heat treatment. This combines the benefits of multiphoton laser fabrication exploiting the method's simplicity and freedom of choice in 3D design. With an additional calcination step this procedure results in the desired micro- and nano-scale 3D glass-ceramic crystalline objects [1]. Proper starting materials selection is the main challenge for convenient laser structuring and formation of predetermined phase composition after the final treatment at high temperatures.

For this work, silicon and zirconium metalorganic polymer precursors of various molar ratios [2] were synthesized. Such mixtures were investigated for the perspective use in 3D laser fabrication. Furthermore, 3D bulk deformation was investigated in tandem with chemical composition and crystallographic phase evolution at different treatment temperatures. The results show that under the proper conditions zircon phase ( $\text{ZrSiO}_4$ ) can be observed (Figure 1(a,b)). Zircon brings high chemical and mechanical stability mainly because of the high coordination of bisdisphenoid  $\text{ZrO}_8$  in a tetragonal structure with  $\text{SiO}_4$  tetrahedrons (Figure 1(d)) [3]. Additionally, it was revealed that the fabricated 3D objects after the heat treatment shrink and retain a complex geometry without any distortion (Figure 1(c)). Therefore this protocol can be applied in the manufacturing of microdevices, where precision and resistance to extremely aggressive chemicals (acids, bases or oxidizing agents) or high-temperature are required. Other zirconium compounds, such as *t*- $\text{ZrO}_2$  (tetragonal) and  $\text{ZrO}_2$  (monoclinic), which are also widely used in modern industry because of their unique properties were also detected.

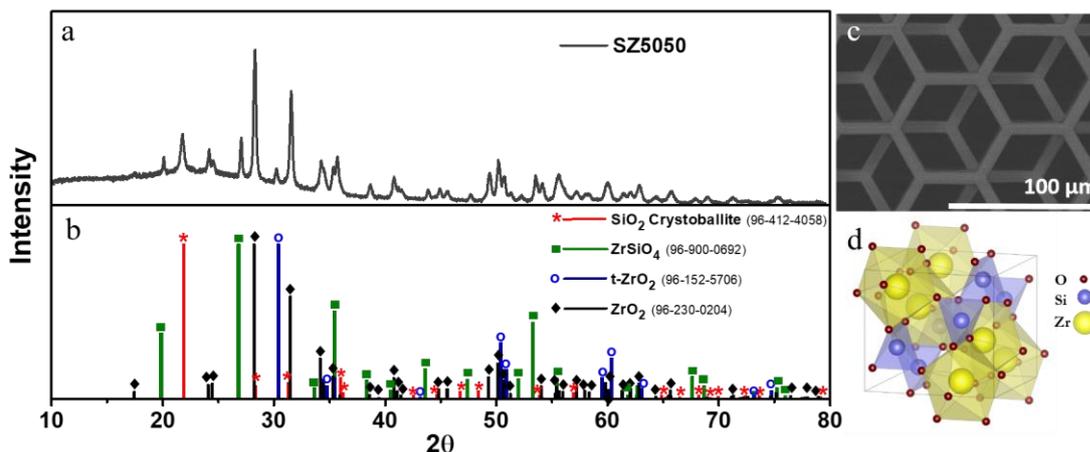


Figure 1. (a) Powder XRD pattern of the SZ5050 sample (photoresist with Si and Zr molar ratio is 1:1) heat-treated at 1400 °C in air; (b) reference data; (c) SEM image of a 3D scaffold treated at 1200 °C in air at ambient pressure; (d) lattice structure of the  $\text{ZrSiO}_4$ .

Overall, the presented results show that laser lithography and thermal post-processing is a powerful combination for resilient multifunctional 3D micro-/nano-scale glassy or ceramic crystalline structures production.

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- [2] A. Ovsianikov, et al., Ultra-Low Shrinkage Hybrid Photosensitive Material for Two-Photon Polymerization Microfabrication. *ACS Nano*; 2, 2257-2262; (2008).
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