Additive Manufacturing of 3D Luminescent ZrO$_2$:Eu$^{3+}$ Architectures

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1. Introduction

Materials doped with luminescent lanthanides have found applications in lasers, displays, lighting, and optical fibers,[1] with advanced applications in the field of bioimaging,[2] light-emitting diodes,[3] luminescence thermometry,[4] theragnostic,[5] microlasers,[6] and waveguides.[7] Such a variety of applications is due to the lanthanide optical properties that stem from their electronic configurations.[7,8] The underlying ladder-like energy levels enable radiative transitions with emissions ranging from ultraviolet to near-infrared.[7–9] Such radiation has a long-lived 4f–4f transition, observed when evaluating lanthanides resulting in sharp narrowband emission. This light emission can be supported even when incorporating the lanthanide ion in a dispersion medium that acts as a host matrix with diverse functionalities.[7,9]

Two host matrix types for lanthanide ions are identified, namely, organic[10] and inorganic materials.[7,11] Inorganic materials have high lattice-binding energy combined with rigidity; thus, in most cases, they show greater chemical and thermal resistance and photostability against continuous excitation than organic materials.[7,8] Highly crystalline inorganic host matrices are typically preferred to reduce point defects emissions. Hence, attention should be given to the crystallinity of the host material and the nonradiative multi-phonon relaxation caused by the crystal lattice.[9] In practice, low phonon energy hosts are preferred to utilize the luminescent activator effectively.[11] However, the commonly used SiO$_2$ ($=1100$ cm$^{-1}$ stretching vibration) presents low lanthanide solubility,[12,13] leading to cluster formation at high dopant contents (10$^{18}$ cm$^{-3}$),[14] quenching the lanthanide emission.[13] In photonics, a substitute for SiO$_2$ is ZrO$_2$, which has relatively good transparency in the visible and infrared range and low phonon energy ($=470$ cm$^{-1}$).[12] ZrO$_2$ occurs in three polymorphs, tetragonal, monoclinic, and cubic, denoted t-ZrO$_2$, m-ZrO$_2$, and...
c-ZrO₂ all broadly applied as a host of trivalent phosphors such as Dy³⁺, Eu³⁺, Gd³⁺, Tb³⁺, and Tm³⁺.[35,36] Among these examples, Eu³⁺ exhibits a sharp emission band corresponding to red and orange-red in the color space chromaticity diagram.[17] The characteristics and dynamics of the Eu³⁺ radiative transitions display high sensitivity to the local environment of the ZrO₂ lattice.[18] For t-ZrO₂-hosted Eu³⁺, two emission lines of similar intensities are typically observed, one at ~590 nm (⁵D₀ → ⁷F₁, from unresolved two allowed transitions) and a second at ~606 nm (⁵D₀ → ⁷F₂).[18] Furthermore, depending on the crystal structure, local symmetry results in an emission characteristic, dominated by ⁵D₀ → ⁷F₂ transition within the 611–618 nm range, with one or weaker lines between 577 and 580 nm (⁵D₀ → ⁷F₃) as known for m-ZrO₂.[38] In case of c-ZrO₂, four lines at 575 nm (⁵D₀ → ⁷F₀), 590 nm (⁵D₀ → ⁷F₁) 607 nm (⁵D₀ → ⁷F₂), and 636 nm (⁵D₀ → ⁷F₃) are observed.[19,20] From these examples, it is clear that emission characteristics of Eu³⁺ can be tuned as a function of the ZrO₂ crystal structure.

Several chemical methods have produced crystalline ZrO₂-hosted Eu³⁺ (ZrO₂:Eu³⁺). These include coprecipitation,[21] hydrothermal,[22] solvothermal,[23] and sol-gel method,[24] leading to nanoparticle formation.[25] Selected examples of ZrO₂:Eu³⁺ of morphologies different than particles include thin films,[26] inverse opals,[27] nanotube arrays,[25] xerogels,[28] and nanofibers.[29] However, a production process of 3D-architected ZrO₂:Eu³⁺ that combines micro(nano)structural features which can be readily integrated into standard cleanroom process flows has not yet been reported.

A way forward is additive manufacturing (AM). AM has the advantage of high processability and can produce 3D luminous architectures.[10,31] Among the AM processes allowing genuinely 3D fabrication of complex structures, two-photon lithography (TPL) has emerged as a state-of-the-art method that permits structural shaping with sub-micrometer precision bridging the gaps between the micro and nanoscale.[32–34] In TPL, the focused femtosecond laser radiation is applied to generate radicals or cations locally, initiating two-photon polymerization of negative-tone photoresists, which solidify in desired areas only.[34,35] Micro- and nano-objects of virtually any arbitrary geometry can be manufactured by rastering the position of the focal spot within the photoreactor in 3D.[34]

In practice, TPL is primarily utilized to fabricate structures from commercially available organic resins, limiting the application scope.[34] New material combinations must be explored to unleash the full potential of TPL and enable the 3D printing of metals, metal oxides, and ceramics to foster the manufacturing of multifunctional materials.[34] Thus far, two main strategies have been implemented for manufacturing such 3D materials using TPL: i) the ex situ approach based on the functionalization of polymeric structures after their photopolymerization, and ii) direct printing using tailor-made resins.[37,39]

For the (i) ex situ approach, the 3D-printed lattices act as templates. The lattice is conformally coated with a metal, metal oxide, or ceramic material to obtain composite core–shell structures. Methods like atomic layer deposition (ALD),[30,31] electrodeposition,[32] or electroless plating[33,34] are typically used to coat such 3D printed architectures. Examples of the deposited layers include Al₂O₃,[35] TiN,[38] ZnO,[39] TiO₂,[41,46] CoNi,[42] or Ag.[44] Upon removal of the organic constituents of the sacrificial lattice, e.g., with oxygen plasma, through a small opening, hollow-beam structures (e.g., Al₂O₃) can be achieved.[38,47]

For route (ii), direct printing with a tailor-made resin approach, either nanofilled or organic–inorganic resin, is used. For nanofilled resins, nanoparticles (NPs) are dispersed in a compatible monomeric matrix via stirring. Usually, the resins are filled with metal or metal oxide nanoparticles to modify the electric, magnetic, or optical properties.[37,48,49] One of the identified limitations of the nanofiller-based approach is that the photolithography process is affected by the NPs properties. Illumination of the NPs dispersed in resins can provoke light scattering affecting the final 3D-printed architecture.[50,52] Furthermore, as the structure dimensions increase (going from voxel clusters to longer beams), high nanofiller loadings may be required, leading to the promotion of light scattering and compromising the lateral resolution during printing.[52] These disadvantages, in practice, render the nanofiller resins unsuitable for the fabrication of complex 3D architectures of fine feature sizes.[31] Organic–inorganic resins free of nanofillers have been extensively investigated and developed to circumvent these limitations.[39,44,55]

Preparing a custom-made photosensitive organic–inorganic resin is laborious since a one-pot synthesis process is not trivial.[39] Typically, organic–inorganic resins incorporate different polymerizable condensation products between the adequate metal- or metalloid-alkoxides and (meth)acrylic acid. The composition of the material obtained after thermal treatment is very much dependent on the polymerized monomeric species. Including metals or metalloids in the organic–inorganic resin matrix and controlling the atmosphere during annealing provides sufficient versatility for producing 3D-printed structures of the desired composition.[56] For example, pyrolysis of crosslinked acrylate siloxanes in N₂ yields SiC,[57] whereas annealing in air results in the formation of SiOC.[58] Other compositions have been reported using hybrid sol-gel resins containing more than one metal or a metalloid, such as an acrylate siloxane complex with zirconium[59] or germanium.[60] Besides the monomers based on the silicon-oxygen backbone, the availability of resins fostering fabrication of certain dopant-free metal-oxides (e.g., SnO₂,[61] TiO₂,[52,62] ZnO),[55] may turn out to be advantageous for tuning the electronic and optical properties of the self-miniaturized polycrystalline 3D-printed structure.[63]

To date, the fabrication of sub-micrometer silicon-free zirconia using organic–inorganic resins via TPL has not been achieved.[64] Although Buchegger et al. reported the fabrication of polymeric woodpile architectures by stimulated emission depletion lithography, the applied resin contained up to 5% of the methacrylate-substituted zirconium oxo cluster [Zr₂O₂(OMc)₁₂]. The study was dedicated to partially replacing the methacrylate ligands in Zr₂O₂(OMc)₁₂ to foster the later thiol-driven functionalization of the resultant inorganic–organic hybrid.[65] It should be noted that the printed structures were not annealed, and the highest Zr₂O₂(OMc)₁₂ applied loading corresponds to ~1.3 wt% of Zr. Structures printed from the commercially available SZ2080 resin, which contains both Si and Zr, could thus far be transformed into inorganic glass-ceramic composed of cristobalite and tetragonal zirconia.[59,60] In retrospect, silicon-free zirconia can be the next steppingstone to manufacture well-dispersed red-emitting 3D-printed ZrO₂ structures.
This work presents the fabrication of silicon-free 3D zirconia microstructures using a custom-made organo-metallic acrylic resin compatible with the two-photon lithography process. The additively manufactured 3D metal-organic polymeric networks are annealed in atmospheric air in a chamber oven, which removes organic components and forms ZrO2 replicas. The annealing of the printed structures in the air at 600 °C results in the formation of t-ZrO2. In the following step, t-ZrO2 is gradually transformed with a temperature ramp-up to yield m-ZrO2 at 1050–1200 °C. The functionality of our ZrO2-photosensitive is assessed with the incorporation of Eu3+, enabling tuning not only the chemical composition of obtained ZrO2 3D structures but also their optical properties. The addition of 3 mol% of Eu3+ containing salt to the resin eases the formation of ZrO2:Eu3+. Optical properties of the ZrO2:Eu3+ printed structures are investigated using cathodoluminescence (CL). For the undoped t-ZrO2, multiple emission bands within 1.65–3.5 eV and m-ZrO2 in the 2.3–2.9 eV range are detected. The fabricated m-ZrO2:Eu3+ and t-ZrO2:Eu3+ structures exhibit characteristic intense 5D0→7F1 and 5D0→7F2 transitions. The orange-red emission from the m-ZrO2:Eu3+ 3D architecture is showcased using wide-field fluorescence microscopy. Our approach promotes the creation of ZrO2 of tunable chemical composition via a one-pot resin preparation process. From a broad perspective, our AM approach can expand the ongoing trend of dimensionally refined functional luminescent materials, uniting materials science with optoelectronics.

2. Results and Discussion

A resin allowing the AM of Si-free Eu-doped ZrO2 microstructures of sub-micrometer feature sizes has been developed. First, the control of the crystallographic phase of polymer-derived ZrO2 microstructures is presented. Next, the resin doping with Eu is highlighted, enabling the fabrication of ZrO2:Eu3+ luminescent microstructures.

2.1. Additive Manufacturing of t-ZrO2 and m-ZrO2 Microarchitectures

Zirconia 3D architectures are fabricated using a custom organic-inorganic resin suitable with two-photon lithography. First, zirconium acrylate (ZrA) is dissolved in N,N-dimethylacetamide (DMAc), and dichloromethane (DCM) in the presence of acrylic acid (AA). Then, a multifunctional crosslinking agent, pentae-rythritol triacrylate (PETA), and a two-photon photoinitiator, 7-Diethylamino-3-thienoyl coumarin (DETC), are added to the mixture (Figure 1a). DCM is used to accelerate the dissolution of zirconium acrylate and is removed under reduced pressure upon the dissolution of ZrA and DETC. The resulting orange-yellow solution contains ~0.2 × 10⁻³ m of Zr and 2.2 wt% of the photoinitiator. The DMAc is selected due to the low vapor pressure and the polar character allowing the dissolution of various inorganic and organometallic salt additives.⁶⁶,⁶⁷

The prepared organic–inorganic resin is drop-casted onto a glass slide and covered with an 8 × 8 mm silicon wafer diced placed on two polyimide spacers (Figure 1b). Such a configuration allows retaining resin within the working distance of the commercial two-photon lithography system (Photonic Professional GT, Nanoscribe). The various 3D microarchitectures (gyroid, octet-truss lattice, supported buckyball) are printed directly on silicon substrates using TPL (Figure 1b) and later developed in dimethyl sulfoxide (DMSO) and isopropanol (IPA) for removal of the non-cured resin. Subsequently, the structures are annealed in atmospheric air in a chamber oven at 600, 750, 900, 1050, and 1200 °C for 1 h (Figure 1d).

Figure 1. Fabrication route of 3D zirconia and europium-doped zirconia microstructures using two-photon lithography. a) Preparation of organic–inorganic resin by dissolving ZrA, DETC, and PETA in AA, DMAc, and DCM. a’) EuOAc × H₂O is added as a resin dopant for the Eu-containing resin. b) Additive manufacturing 3D pre-ceramic structures (ZrO₂ or ZrO₂:Eu³⁺) on a silicon substrate via TPL using the custom organic–inorganic resin. c) UV-curing of the custom resins. d) Annealing of the 3D pre-ceramic structures and cured resins at 600–1200 °C for 1 h, resulting in isotropically shrunken ZrO₂ replicas, or powder, respectively. e) Cathodoluminescence of the ZrO₂:Eu³⁺ 3D structures and the ZrO₂:Eu³⁺ ceramic powder.
The process is associated with \(\approx 60\%\) isotropic linear shrinkage and yields self-miniaturized solid ZrO\(_2\) replicas. Scanning electron microscopy (SEM) images of 3D-printed annealed structures are shown below (Figure 2a–d). A representative SEM image of the pre-ceramic gyroid is presented in Figure S1a (Supporting Information). The annealing at 600 °C results in the formation of finely grained \(t\)-ZrO\(_2\), presented for an octet-truss lattice in Figure 2a. The annealing at 900 °C results in partly transformed ZrO\(_2\), associated with the growth of the grains, depicted for a buckyball (Figure 2b), octet truss lattice (Figure 2c), and gyroid (Figure 2d) structures. The octet truss lattice thermally processed at 1200 °C consists of crystallites of 224.3 ± 65.4 nm average diameter (Figure S2a–c, Supporting Information). The spatial chemical composition of the fabricated annealed structures determined with energy-dispersive X-ray spectroscopy (EDS) is presented in Figure 2e. Both O and Zr are uniformly distributed throughout the architecture. Si is only present in the substrate and absent in the printed structure. Individual Si-indexed pixels are present in the areas matching the cavities and support layer in the gyroid structure.
attainable for the typical reactive volumes for characteristic X-rays in EDS analysis.\textsuperscript{[68]} The annealing of Si substrates on which structures are printed results in surface oxide layer formation, as confirmed in the SEM-EDS maps showing Si and O distribution (EDS (Figure 2e). The thickness of SiO\textsubscript{2} depends on the temperature, duration of the annealing, and atmosphere, and may reach hundreds of nanometers.\textsuperscript{[69]} SiO\textsubscript{2} growth is not identified to be detrimental to the adhesion of the printed 3D structures under the range of conditions applied during the annealing step. The structural integrity of a manufactured 3D octet-truss ZrO\textsubscript{2} lattice annealed at 600 °C is inspected with focused ion beam (FIB) tomography (Figure 2f). The beams are solid throughout the architecture, indicating adequate 3D design slicing parameters for a TPL process. The periodic lattice morphology is preserved, and no discernible regions with broken or discontinuous features can be found, as confirmed in Video S1 (Supporting Information).

The phases of ZrO\textsubscript{2} are known to possess different crystallographic and optical properties. From this viewpoint, accurate control of the 3D structure crystallinity is crucial for realizing specific functionalities. The influence of annealing on the crystallinity of the polymer-derived ZrO\textsubscript{2} replicas of 3D-printed structures is analyzed using confocal Raman spectroscopy at 532 nm excitation wavelength (Figure 3a, labeled in red). Samples annealed at 600, 750, 900, 1050, and 1200 °C are characterized. The spectrum acquired for the sample annealed at 600 °C shows vibrational modes at 146 cm\textsuperscript{-1} (B\textsubscript{1g}), 267 cm\textsuperscript{-1} (E\textsubscript{g}), 314 cm\textsuperscript{-1} (B\textsubscript{1g}) and two broad bands at 460 cm\textsuperscript{-1} (E\textsubscript{g}), and 642 cm\textsuperscript{-1} (E\textsubscript{g}), assigned to the t-ZrO\textsubscript{2} phase.\textsuperscript{[70–72]} For samples annealed at 750 °C, two additional shoulders at 476 and 596 cm\textsuperscript{-1} are observed, which may indicate the appearance of trace amounts of m-ZrO\textsubscript{2}.\textsuperscript{[71–73]} The spectrum registered for structures annealed at 900 °C is dominated by t-ZrO\textsubscript{2} content. The observed bands are likely broadened due to the superposition with m-ZrO\textsubscript{2} signals. Upon deconvolution (Figure S3, Supporting Information), vibrational modes of t-ZrO\textsubscript{2} at 148 cm\textsuperscript{-1} (B\textsubscript{1g}), 268 cm\textsuperscript{-1} (E\textsubscript{g}), 464 cm\textsuperscript{-1} (E\textsubscript{g}), 606 cm\textsuperscript{-1} (B\textsubscript{1g}), and 649 cm\textsuperscript{-1} (E\textsubscript{g}) are recognized. The contributions at 321 cm\textsuperscript{-1} (A\textsubscript{g}) and 524 cm\textsuperscript{-1} (B\textsubscript{1g}) can likely be assigned to m-ZrO\textsubscript{2}.\textsuperscript{[70–72]} The contributions of m-ZrO\textsubscript{2} are of minor intensity, and their location is strongly superposed with other narrowly distributed vibrational modes of ZrO\textsubscript{2}. Due to the open lattice character of the structures, a background peak at 521 cm\textsuperscript{-1} originating from the crystalline Si substrate (Figure S4, Supporting Information) may be observed during signal acquisition, which may partially overlap with B\textsubscript{1g} m-ZrO\textsubscript{2}.\textsuperscript{[74]} Spectra registered for samples calcined at 1050 and 1200 °C are characterized by the presence of typical m-ZrO\textsubscript{2} vibrational modes at 172 cm\textsuperscript{-1} (B\textsubscript{1g}), 185 cm\textsuperscript{-1} (A\textsubscript{g}), 215 cm\textsuperscript{-1} (B\textsubscript{1g}), 298 cm\textsuperscript{-1} (B\textsubscript{1g}), 302 cm\textsuperscript{-1} (B\textsubscript{1g}), 328 cm\textsuperscript{-1} (B\textsubscript{1g}), 340 cm\textsuperscript{-1} (A\textsubscript{g}), 377 cm\textsuperscript{-1} (A\textsubscript{g} + B\textsubscript{1g}), 471 cm\textsuperscript{-1} (A\textsubscript{g}), 497 cm\textsuperscript{-1} (B\textsubscript{1g}), 532 cm\textsuperscript{-1} (B\textsubscript{1g}), 555 cm\textsuperscript{-1} (A\textsubscript{g}), 612 cm\textsuperscript{-1} (B\textsubscript{1g}), and 632 cm\textsuperscript{-1} (A\textsubscript{g}), and the absence of discernible t-ZrO\textsubscript{2} signals.\textsuperscript{[70–72]} It can be therefore concluded that the annealing at 600 and 750 °C yields t-ZrO\textsubscript{2}, whereas the thermal treatment at 1050° and 1200 °C results in m-ZrO\textsubscript{2}. At 900 °C, a partly transformed product containing mostly t-ZrO\textsubscript{2} and trace m-ZrO\textsubscript{2} is synthesized.

The influence of annealing on the crystallinity of the resin-derived ZrO\textsubscript{2} powders is investigated using confocal Raman spectroscopy and X-ray powder diffraction (XRD) to cross-validate the results found for the 3D-ZrO\textsubscript{2} structures analyzed with Raman. The resin is cured using a conventional 36 W UV lamp (Figure 1b). The portions of polymerized resin are pulverized in an agate mortar and annealed for 1 h at 600, 750, 900, 1050, and 1200 °C (Figure 1d). The XRD results (Figure 3b) for samples annealed at 600 and 750 °C give a characteristic t-ZrO\textsubscript{2} (P\textsubscript{4}3/mnc space group) diffractogram with dominant (101) diffraction at 30.3°.\textsuperscript{[55–57]} Partly transformed zirconia containing ∼67% of m-ZrO\textsubscript{2} phase is harvested after treatment at 900 °C (Figure S3, Supporting Information), confirmed by the presence of (111) t-ZrO\textsubscript{2} diffraction at 30.3° and emergence of the distinctive m-ZrO\textsubscript{2} peaks at 28.3° (T111) and 31.5° (111).\textsuperscript{[76]} The annealing at 1050 and 1200 °C results in the complete

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**Figure 3.** a) Confocal Raman spectroscopy spectra of 3D-printed ZrO\textsubscript{2} structures annealed at 600, 750, 900, 1050, and 1200 °C for 1 h; samples excited at 532 nm. Labels: blue – powders, red – 3D structures. B\textsubscript{1g} and E\textsubscript{g} are t-ZrO\textsubscript{2} vibrational modes, and B\textsubscript{1g} and A\textsubscript{g} m-ZrO\textsubscript{2}. Asterisk (*) denotes the Si substrate signal. b) XRD diffractograms for ZrO\textsubscript{2} powders obtained from pulverized UV-cured Zr-rich resin annealed at 600, 750, 900, 1050, and 1200 °C for 1 h. Labels: t for t-ZrO\textsubscript{2}, m for m-ZrO\textsubscript{2}.
transformation to $m$-$\text{ZrO}_2$ ($P2_1/c$ space group).[78] No phase lines typical for discernible impurities, $t$-$\text{ZrO}_2$, $\epsilon$-$\text{ZrO}_2$, or oxygen-deficient $\text{ZrO}_2$, are observed.[89]

For confocal Raman spectroscopy, the powder samples are cast on a 10 $\times$ 10 mm sapphire substrate and characterized with a 532 nm excitation laser. The spectroscopic results obtained for powders and $\text{ZrO}_2$ 3D structures are in good agreement (Figure 3a, labeled in blue). Similar phase transformation temperatures for the 3D-printed $\text{ZrO}_2$ structures have been found for powders and layers obtained from carbon-rich mixtures via a sol-gel process[79,80] or for electrospun nanofibers.[75,81] To this end, 3D-printed $t$-$\text{ZrO}_2$ samples annealed at 600 and 750 °C and the 3D-printed $m$-$\text{ZrO}_2$ treated at 1050 and 1200 °C are comparable to the powder $\text{ZrO}_2$. From these results, it is fair to say that confocal Raman spectroscopy and XRD help to cross-compare the results of the 3D-printed $\text{ZrO}_2$ structures.

The intrinsic luminescent properties of the $t$-$\text{ZrO}_2$ and $m$-$\text{ZrO}_2$ are studied with CL for representative buckyballs annealed at 600 and 1200 °C. Powders obtained from the resins under the same annealing conditions are used as references. Figure 4a,e shows SEM and panchromatic CL images of a $\text{ZrO}_2$ buckyball, thermally treated at 600 °C. All regions of the 3D structure generate luminescence in agreement with its high crystallinity. Furthermore, images acquired at high magnifications reveal a grain structure in the $\text{ZrO}_2$ buckyballs, as shown in Figure 4e,f, with some grains exhibiting a low CL intensity (see arrows) that we attribute to a low density of radiative centers. Point defects, such as oxygen vacancies ($V_0$), typically act as radiative centers in $t$-$\text{ZrO}_2$,[83] which could be present at low density in some grains of buckyballs. CL images obtained from a $\text{ZrO}_2$ buckyball annealed at 1200 °C reveal a similar CL distribution, as shown in Figure 4c,d,g,h.

CL spectra obtained from $\text{ZrO}_2$ buckyballs thermally treated at 600 and 1200 °C show broad emissions centered at about 2.9 and 2.6 eV, composed of several components as shown in Figure 4i,j. The components calculated by the deconvolution of the CL spectra using Gaussian curves are centered at 1.65, 2.3, 2.6, 2.9, 3.2, and 3.5 eV for $\text{ZrO}_2$ annealed at 600 °C and centered at 2.3, 2.6, and 2.9 eV for $\text{ZrO}_2$ buckyballs annealed at 1200 °C, to match the energy of defects-related emissions reported by other authors.[79,83–86] The full width at half maximum (FWHM) of these components is adjusted to obtain a fitting value for the coefficient of determination nearest to unity. The values obtained for this parameter are 0.995 and 0.997 after fitting the CL spectra of $\text{ZrO}_2$ buckyballs annealed at 600 and 1200 °C by assigning an FWHM of 0.35 eV to each Gaussian component. It is essential to consider that the FWHM usually simultaneously represents the homogeneous and inhomogeneous broadening of the linewidth of an electronic transition. Electron–phonon coupling in perfect crystals generates the homogeneous or natural broadening (represented with a Lorentzian curve). In contrast, the inhomogeneous broadening (commonly represented with a Gaussian curve) is generated by crystallinity disorder associated with impurities, anti-site defects, or vacancies.[87,88] In this work, we have assigned the same FWHM value of 0.35 eV for all defect-related emissions in $\text{ZrO}_2$ buckyballs, attributing that each corresponds to individual electronic transition with a comparable inhomogeneous broadening. The component of 3.5 eV has been reported by Cong et al.[84] proposing an origin to electronic transitions from excited (F*) centers and the valence band (VB). An oxygen vacancy ($V_0$) physically represents a well-potential of finite height into a crystal with quantized energy levels that one or two electrons can occupy. An F* center is an oxygen vacancy ($V_0$) with a single trapped electron in such well-potential occupying the ground-state energy and exhibiting an s-like wave function, which can be promoted to the first excited state to exhibit a p-like wave function. This last excited state is known as an excited (F*) center.[89,90] Electrons trapped in $V_0$ states can recombine with holes to generate electromagnetic radiation or remain in the lattice modifying its charge distribution. For example, Kumar et al. previously reported that Zr$^{4+}$ ions abutting bulk $V_0$ could capture electrons forming Zr$^{3+}$ species.[91] The band of 3.2 eV has been reported by Wang et al. in $t$-$\text{ZrO}_2$ nanopowders, associating its generation to the presence of F* centers.[92] For the component of 2.9 eV, Lin et al. have demonstrated by electronic paramagnetic resonance (EPR) measurements that its origin is due to the presence of carbon impurities as interstitial defects ($C_i$) in $t$-$\text{ZrO}_2$ powders, besides that the formation of $V_0$ in the lattice of $m$-$\text{ZrO}_2$ generates the 2.6 eV emission.[79] However, emission of 2.6 eV also has been reported in $m$-$\text{ZrO}_2$ powders by Ashraf et al., proposing an origin to electronic transitions between the levels generated by the excited F* and F* states.[89] Finally, the component of 2.3 eV could correspond with the emission of 2.2 eV for $t$-$\text{ZrO}_2$ nanoparticles reported by Zhang et al. They attribute it to the presence of carbon impurities ($C_i$), demonstrating that the emission is tuned in energy with the amount of carbon incorporated in such nanostructures.[86] The additional monochromatic CL images of $t$-$\text{ZrO}_2$ and $m$-$\text{ZrO}_2$ buckyballs obtained at 2.6 and 2.9 eV are provided in Figure S6 (Supporting Information). The presence of carbon-based impurities is highly probable for polymer-derived ceramics[86] and has been previously observed for ZnO microstructures fabricated via TPL.[53] Figure 4i reveals that CL emission from $m$-$\text{ZrO}_2$ buckyballs only exhibits the components of 2.3, 2.6, and 2.9 eV, where the second dominates the spectrum and can be associated with the presence of carbon impurities ($C_i$). The absence of the 3.2 and 3.5 eV emissions in $m$-$\text{ZrO}_2$ buckyballs indicates that thermal treatment at 1200 °C does not eliminate carbon impurities ($C_i$) but suppresses $V_0$ point defects. Lin et al. have computed structural models of carbon impurities ($C_i$) in $t$-$\text{ZrO}_2$ and oxygen vacancies ($V_0$) in $m$-$\text{ZrO}_2$, considering that they are present in each of these phases. They demonstrate that the bandgap of $t$-$\text{ZrO}_2$ with $C_i$ is slightly larger than that of $m$-$\text{ZrO}_2$ with $V_0$.[90]
Figure 4. a) SEM and e) panchromatic CL images of an undoped ZrO₂ buckyball thermally treated at 600 °C. b) SEM and f) CL images of the grain structure reveal an inhomogeneous luminescence. c) SEM and g) panchromatic CL images of an undoped ZrO₂ buckyball thermally treated at 1200 °C. d) SEM, h) panchromatic CL image. Scale bars represent (a–d) 3 µm and (e–h) 1 µm. Deconvoluted normalized CL spectra of the undoped i) t-ZrO₂ and j) m-ZrO₂ buckyballs thermally treated at 600 and 1200 °C. Deconvoluted CL spectra of the undoped k) t-ZrO₂ and l) m-ZrO₂ powders thermally treated at 600 and 1200 °C.
2.2. Additive Manufacturing of Eu-Doped t-ZrO2 and m-ZrO2 Luminescent Microarchitectures

After successfully fabricating t-ZrO2 and m-ZrO2 3D-structures, we investigate the possibility of doping with Eu3+ by adding europium acetate hydrate (EuOAc $\times$ H2O) to the resin (3 mol% of Eu, relative to Zr). First, the influence of doping on the crystallographic phase of ZrO2:Eu powders derived from the UV-cured resin annealed at 600 and 1200 °C is discussed below. XRD (Figure S7, Supporting Information). We conclude that, at least for the tested concentrations, doping with Eu does not alter the resulting crystallographic phases of ZrO2 or yield in at least for the tested concentrations, doping with Eu does not alter the resulting crystallographic phases of ZrO2 or yield in a different product. Characteristic t-ZrO2 pattern with dominant (101) t-ZrO2 reflection at 30.3° for the powder thermally treated at 600 °C is preserved.[75,76] For the sample annealed at 1200 °C a distinctive m-ZrO2 diffractionogram with the most intense peaks at 28.3° ($\bar{1}11$) and 31.5° (111) is observed.[76] The Eu content estimated via EDS is 3.4% wt. (Zr 26.1, O 7.1, C 4.0% wt). The presence of carbon impurities in powder samples reinforces the conclusions on their influence on observed emissions for t-ZrO2 and m-ZrO2. X-ray photoelectron spectroscopy (XPS) analysis is assessed to confirm the chemical state of Eu (Figure S8, Supporting Information). The oxidation state of the dopant in ZrO2 powder annealed at 1200 °C is found, which potential origin is discussed below.

Next, ZrO2:Eu3+ 3D-structures are manufactured via TPL following the same protocol as for ZrO2 (Figure 1a). The developed, printed buckyballs are annealed at 600 and 1200 °C for 1 h. Figure 5a–f shows SEM and CL images obtained for the point-defect (2.9 and 2.6 eV) and Eu3+ ions (2.1 eV) emissions for t-ZrO2:Eu3+ and m-ZrO2:Eu3+ buckyballs. These images reveal a homogeneous CL distribution for the V0-related 2.9 eV emission (Figure 5b) and C-related 2.6 eV (Figure 5f) emission in t-ZrO2:Eu3+ and m-ZrO2:Eu3+ buckyballs, respectively. In addition, brighter regions at the edges of the buckyballs for the Eu3+ emission of 2.1 eV (Figure 5c,f) reveal that the dopant is mainly present at the edges of such 3D structures. This contrast could also be ascribed to a more intense CL emission associated with the higher specific free surface of the buckyball at the edges; however, since this effect is not observed in the CL images obtained at 2.9 and 2.6 eV (Figure 5b,e), we conclude that the CL image obtained at 2.1 eV represents the Eu3+ distribution. Figure 5j shows CL spectra from t-ZrO2:Eu3+ and m-ZrO2:Eu3+ buckyballs, exhibiting strong emissions generated by transitions between levels 5D0 and 7FJ of Eu3+. CL spectrum of the t-ZrO2:Eu3+ buckyball also shows a weak broad emission with components of 2.6, 2.9, 3.2, and 3.5 eV (Figure 5j), suggesting that Eu3+ ions incorporated as a substitutional impurity (Eu2+) in the t-ZrO2 lattice without modifying its defect structure. Furthermore, Figure 5j also reveals that Eu3+ ions incorporated in the m-ZrO2 quench the emissions associated with point-defects (inset in Figure 5j). CL measurements obtained from ZrO2:Eu3+ powders also reveal electronic transitions corresponding with Eu3+ ions for tetragonal and monoclinic phases, as shown in Figure 5k. In contrast to ZrO2:Eu3+ buckyballs, the m-ZrO2:Eu3+ powders revealed an increase in the emission intensity of 2.3, 2.6, and 2.9 eV, suggesting that the fabricated m-ZrO2:Eu3+ buckyballs possibly contain fewer oxygen vacancies. However, we do not discard the possibility that the increase of the intensity of these three bands could also be correlated with a partial reduction of Eu3+ species to Eu2+ in the m-ZrO2:Eu3+ powder because the Eu2+ signals generated by electronic transitions between the levels 4f55d1 and 4f5(S5/2) can overlap with peaks typically observed for the luminescence of intrinsic ZrO2 defects within the 3.18–2.38 eV range.[92] These findings may correspond with small quantities of Eu2+ observed in the XPS results for m-ZrO2:Eu3+ powder (Figure S8d, Supporting Information), not observed in the Eu-doped m-ZrO2 buckyballs. The reduction of Eu3+ to Eu2+ can be readily induced in organic solvents by femtosecond laser radiation and UV light.[91,94] In practice, the extent to which resin curing affects the Eu2+ population seems limited. In our study, CL emissions are related to Eu3+ species observed in Eu-doped m-ZrO2 powder. The Eu2+ formation likely proceeds during the thermal processing. Various mechanisms have been discussed for the Eu3+ reduction to Eu2+ in mixed oxide host matrices.[95] We propose that the reduction of Eu3+ in m-ZrO2 powder may proceed from the defect centers during annealing.[96] Upon increasing the annealing temperature in the air from 600 to 1200 °C, the Vp population reduces, which indirectly indicates they may participate in the Eu2+ formation. Although our work is dedicated to 3D printing ZrO2:Eu structures, it is also a pioneer in using photopolymerization and metal–organic monomers to obtain bulk powders. Further dedicated studies on powder phosphors derived from the carbon-rich precursors should help better interpret the Eu2+ reduction phenomenon.

Finally, the optical emission of the representative m-ZrO2:Eu3+ buckyball is investigated with wide-field fluorescence microscopy. The 3D structure is excited using a 405 nm source resulting in orange-red emission (Figure 5g), a color that agrees with the transitions between levels 5D0 and 7F1 of Eu3+ observed with CL. The uniformity of the emission from the 3D phosphor in the lateral direction is assessed (Figure 5h), showing a pattern resembling the morphology of the buckyball. A 3D reconstruction of the 3D structure is presented in Video S2 (Supporting Information).

3. Conclusions

We have manufactured 3D silicon-free ZrO2 microstructures with sub-micrometer feature sizes for the first time. The influence of the annealing temperature (600, 750, 900, 1050, 1200 °C) was studied using XRD and Raman. The presented method yields t-ZrO2 and m-ZrO2 architectures. The microstructures undergo ~60% isotropic shrinkage after annealing, compared to the initial dimensions of the printed pre-ceramic architectures. With the increase of the annealing temperature, the gradual growth of the grains building the microstructures is observed with the aid of SEM, as expected on the premise of XRD peak narrowing for the reference powders. The cathodoluminescence study reveals a broadband emission in the 1.65–3.5 eV range for t-ZrO2 and within the 2.3–2.9 eV for m-ZrO2, which unveils the lattice structure of t-ZrO2 contains oxygen vacancies and carbon impurities, while m-ZrO2 predominantly the latter ones.

The developed resin is compatible with europium acetate hydrate, used as a dopant to introduce 3.4 wt% of Eu3+ into...
Figure 5. a) SEM and monochromatic CL images obtained at b) 2.9 eV and c) 2.1 eV of a ZrO$_2$:Eu$^{3+}$ buckyball thermally treated at 600 °C. d) SEM and monochromatic CL images obtained at e) 2.6 eV and f) 2.1 eV of a ZrO$_2$:Eu$^{3+}$ buckyball thermally treated at 1200 °C. Scale bars represent 2 µm. g) Digital camera image showing orange-red emission from the m-ZrO$_2$:Eu$^{3+}$ buckyball upon excitation at 405 nm, collected from the microscope eyepiece. h) Color-coded z-stack image of the m-ZrO$_2$:Eu$^{3+}$ buckyball emission upon excitation at 405 nm; color scale: blue corresponds with the emission from the top, green from the middle, and red from the bottom of the buckyball; scale bar represents 3 µm. Normalized CL spectra of the Eu-doped ZrO$_2$ buckyballs thermally treated at i) 600 °C and j) 1200 °C revealing a quenching of the point defect bands. Deconvoluted CL spectra of the Eu-doped ZrO$_2$ powders thermally treated at k) 600 °C and l) 1200 °C.
the ZrO$_2$ matrix. The doping of ZrO$_2$ with Eu does not affect the resulting crystallographic phase of ZrO$_2$; fabrication of t-ZrO$_2$:Eu$^{3+}$ and m-ZrO$_2$:Eu$^{3+}$ microstructures is feasible with the presented approach. The 3D-printed ZrO$_2$:Eu$^{3+}$ buckyballs annealed at 600 and 1200 °C are highly efficient phosphors. Interestingly, Eu$^{3+}$ is localized mainly at the edges of these 3D structures, which can be observed as brighter regions in the CL images obtained at 2.1 eV, corresponding with the characteristic Eu$^{3+}$ emission. The emission properties of the buckyballs and ZrO$_2$:Eu$^{3+}$ powders are characteristic for the material and in agreement with previously reported components. The t-ZrO$_2$:Eu$^{3+}$ buckyball emissions are dominated with 5D$_0$$\rightarrow$$^7$F$_m$ and 5D$_0$$\rightarrow$$^5$F$_m$ transitions; in the case of the m-ZrO$_2$:Eu$^{3+}$ structure, the latter one is subtly less intense. Upon doping, the defect structure of the t-ZrO$_2$ lattice results in a weak broad emission, the latter one is subtly less intense. Upon doping, the characteristic Eu$^{3+}$ CL images obtained at 2.1 eV, corresponding with the characteristic Eu$^{3+}$ emission. The emission properties of the buckyballs and ZrO$_2$:Eu$^{3+}$ powders are characteristic for the material and in agreement with previously reported components. The t-ZrO$_2$:Eu$^{3+}$ buckyball emissions are dominated with 5D$_0$$\rightarrow$$^7$F$_m$ and 5D$_0$$\rightarrow$$^5$F$_m$ transitions; in the case of the m-ZrO$_2$:Eu$^{3+}$ structure, the latter one is subtly less intense. Upon doping, the defect structure of the t-ZrO$_2$ lattice results in a weak broad emission, the latter one is subtly less intense. Upon doping, the defect structure of the t-ZrO$_2$ lattice results in a weak broad emission, the latter one is subtly less intense. 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Cathodoluminescence: Room temperature CL measurements were conducted using a JEOL JIB-4500 SEM equipped with a Catanon Monochrom detector. An acceleration voltage of 15 kV was applied.

Confocal Raman Spectroscopy (Raman): Raman spectra were obtained using a confocal Raman microscopy system (Alpha 300, WiTec) equipped with a 100×/0.9 NA air objective (MIPlan FL N, Olympus) and 532 nm excitation laser set at 5.0 mW power. Selected samples were additionally excited with 633 and 785 nm lasers at 5.0 mW power. Registered data consist of 30 averaged spectra, each accumulated for 10 s in backscattering geometry using a 600 g mm⁻¹ grating. The data were processed using CrystalSleuth software to remove cosmic rays and reduce background. For 3D-printed structures, additional Si substrate spectra were recorded for each annealing temperature (Figure S4, Supporting Information). The powders obtained from the annealed resins were ground in an agate mortar and characterized on the sapphire substrates.

Wide-Field Fluorescence Microscopy: The sample was positioned facing the objective and mounted on a coverslip (100 μm thickness, 24 mm diameter) with double-sided tape as a spacer. A drop of immersion oil (Nikon) was used between the objective and the coverslip. Micrographs were recorded using a Nikon Eclipse Ti inverted microscope equipped with a Nikon SR Apo TIRF 100 × 1.49 NA oil immersion objective coupled with Andor iXon Ultra 897 camera set at 50 ms exposure time and 50 EMCCD gain. A 405 nm laser (Oxxius) with 800 W cm⁻² irradiance was used for the excitation. The emitted light was separated from the excitation using a quad-band 405/488/561/647 nm dichroic mirror and filtered with the matching fluorescence filter (Semrock). Each camera pixel corresponded to 107 nm in the object plane. The z displacement was provided by a piezoelectric nanopositioner (Nano-Z, Mad City Labs). For each 250 nm mechanical step, four frames were acquired and averaged. The images were processed to reduce the focal shift of the z positions due to the index mismatch, assuming the 0.5 value. A Python code was written to reduce off-focus background by subtracting the local mean value for each frame with 15-pixel Gaussian sigma. The multicolor image was generated with Fiji software by superposing depth color-coded images at various z planes. Finally, the 3D movie was generated with the Fiji 3D Viewer. It should be noted that the image presenting orange-red emission from the m-ZrO₂:Eu³⁺ backscanning excited at 405 nm (Figure 5g) was collected directly from the ocular lens aperture of the fluorescence microscope using a smartphone due to the lack of an RGB camera.

SEM and SEM-EDS: The top-view images of 3D structures were recorded using SEM (Carl Zeiss, Merlin AURIGA CrossBeam Workstation) equipped with Inlens and High-Efficiency Secondary Electron (HE-SE2) detectors. An acceleration voltage of 1.5–2.2 kV was applied. The description of the image processing for display purposes is provided (Figure S10, Supporting Information). Elemental mappings were prepared using an EDS attachment to the SEM system. The data were processed with AzTec (Oxford Instrument) software.

Thermogravimetric Analysis: The weight losses of the cured dried resin placed in platinum crucible were analyzed at a 5 °C min⁻¹ heating rate in the air within a 37–1200 °C range (STA 449 F3, Netzsch).

Tomography: A FIB/SEM dual-beam microscope (Thermo Fisher Scientific, Helios Nanolab 600i) was used for the tomography of the octet-truss lattice. The tomography consists of 139 slices with a spacing of ~80 nm. Milling of the single slices was performed at 30 kV acceleration voltage and with a beam current of 230 pA. The single slices were recorded with a secondary electron detector at an acceleration voltage of 5 kV and a beam current of 0.69 nA. The images were aligned via digital image correlation (DIC) by the microscope software Auto Slice and View 4.0 (Thermo Fisher Scientific).

X-Ray Powder Diffraction: The samples of annealed cured resins were cast on a zero-diffraction plate and characterized with a diffractometer (D2 Phaser, Bruker) (30 kV, 10 mA) equipped with LynxEye detector, using Cu-Kα source radiation at 2θ scan range of 20°–80° with 2.25° min⁻¹ scan speed. The spectra were baseline-corrected using CrystalSleuth software.

X-ray Photoelectron Spectroscopy: XPS measurements were conducted with a SPECS system equipped with a PHOIBOS WAL analyzer using an Al anode. High-resolution spectra were obtained using 300 scans at 0.1 eV sensitivity. Eu-doped m-ZrO₂ powder was quantified with the aid of CasaXPS processing software, and XPS spectra were deconvoluted into Gaussian peaks using a Shirley background. The obtained spectra were calibrated using the C 1s signal (284.6 eV) as reference.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest
The authors declare no conflict of interest.

Data Availability Statement
The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords
additive manufacturing, europium, luminescence, two-photon lithography, zirconia

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