**INTRODUCTION**

The design of optical systems requires balancing trade-offs in system cost and complexity, size, and weight, as well as in meeting schedule, performance, and lifetime requirements. New approaches to optics fabrication continue to emerge, providing access to additional degrees of optical design freedom (1–3).

Conventional lenses are typically made from a uniform composition bulk material, and control of light refraction is dictated by the thickness and surface curvature of the lens. Spherical, cylindrical, aspheric, and similar lenses are readily produced by well-established fabrication methods, such as lap polishing and CNC (computer numerical control)–based finishing. In addition, freeform optics—containing custom complex curvatures with no translational or rotational symmetry—can be fabricated, but usage remains limited due to stringent requirements for surface polishing precision.

Gradient refractive index (GRIN) optics provide an alternative to conventionally finished optics. GRIN optics contain a spatial gradient in material composition, which, in turn, provides a gradient in material refractive index, thereby altering how light travels through the medium. A GRIN lens can have a flat surface figure yet still perform the same optical function as an equivalent conventional lens.

GRIN optics already exist in nature as a result of the evolution of eye lenses. Examples can be found in most species, where the change in refractive index across the eye lens is governed by the varying concentration of structural proteins (crystallins) (4). In squid eyes, crystallins of different sizes form a gel of varying density; this gradient in refractive index combined with curvature allows the lens to naturally compensate for spherical aberrations (5). The ability to fully spatially control material composition and, therefore, optical functionality provides opportunities for GRIN optic design. For example, multiple functionalities could be designed into a single optic, such as focusing combined with correction of common optical aberrations (spherical, coma, astigmatism, etc.). In addition, it has been shown that the use of optics with combined surface curvature and gradients in refractive index has the potential to reduce the size and weight of optical systems (6, 7).

Several approaches to fabricate polymeric GRIN lenses have been reported (8–13). However, certain optical applications require improved environmental stability to maintain function; in these cases, glass is the material of choice. Existing methods for producing GRIN glass include solid diffusion (14–17), sol-gel diffusion (18, 19), and mating and joining preforms (20–22). Diffusion-based approaches are mostly limited to two-dimensional (2D), monotonic composition profiles, and most of these approaches involve challenging, time-consuming steps that are difficult to scale. In contrast, an additive manufacturing route provides options for truly tailored compositions as well as complex shapes and patterns in three dimensions (23, 24). 3D printing of transparent glass has been demonstrated recently by several groups (25–31); however, most of these techniques have not yet demonstrated multimaterial printing of glass with gradient composition and refractive index. Recently, Moore *et al.* (32) have used photopolymerization-induced phase separation of hybrid resins to create glass parts with multiscale porosity by manipulating the intensity of the digital light projection. An early attempt at producing glass with compositional gradients for optical functionality used an ink jetting process to deposit a liquid-phase dopant over a silica powder bed, drying each layer of wetted powder, and repeating layer by layer to produce a dopant concentration profile (33). Although the technique generated glass with measurable dopant concentration profiles, substantial concentration variations (~±10 relative mole percent layerwise along the build direction) were observed over the millimeter scale, attributed to migration during layerwise drying, and optical functionality of the glass was primarily inferred by calculation.

Our group has previously demonstrated a two-stage approach to glass formation that involves extrusion-based 3D printing of silica nanoparticle gels via direct ink writing (DIW), followed by densification of the printed components to glass through heat treatment (34). We have developed printable silica and silica-titania formulations that permit tuning of the glass refractive index and provide control of the ink rheology to enable printing of two separate inks through the same nozzle under the same printing conditions (35, 36).

Here, we show that GRIN glass optics can be produced using multimaterial DIW. The system is equipped with an active micromixer capable of in-line blending of two different inks, allowing 3D printing of green bodies with compositional gradients, which are then consolidated into glass optics with tailored spatial profiles of the refractive index.

**RESULTS**

**3D printing and processing of GRIN glass**

GRIN optics were printed using a DIW setup with an in-line active micromixer nozzle (Fig. 1A). The micromixer consists of two inlets and a rotating mixing element placed inside a nozzle (<1-mm diameter at outlet) (37, 38). The inks are dispensed through the inlets using...
positive displacement and mixed under high shear in the annular region of the mixing nozzle. The ratio of inks in the mixer determines the output composition. By controlling the relative flow rates of the two inks, a desired concentration profile can be programmed into the toolpath. This approach enables printing of functionally graded multimaterial 3D objects.

The green body is printed from inks consisting of silica-titania nanoparticle gels to create prescribed concentration gradients, informed by chosen refractive index changes in the final glass. The gradient composition green body is then thermally treated to remove all solvents, burned out of all traces of organic compounds, and sintered to full density (Fig. 1B). The sintered glass is polished to a flat surface figure. The final glass is a GRIN optic—a flat lens with a spatial gradient in refractive index resulting from the change in the titania dopant concentration (Fig. 1C). The photograph in Fig. 1D depicts the optics’ as-printed shapes and extents after the grinding and polishing removal of ~300 µm each from the upper and lower surfaces. Optics were polished to remove texture from print lines and to achieve surface microroughness <1-nm root mean square (rms), typical for transmissive optics. Note that the fully dense component is all on the order of 1 cm in the largest dimension with thickness ranging from 1 to 5 mm after polishing, depending on the optic.

**Active in-line micromixing of viscoelastic inks**

3D printing of compositional gradients is achieved by printing discretized concentration step profiles. The smoothness of the gradient will depend on the step size; thus, using a smaller nozzle will produce a finer profile. However, the choice of nozzle size also depends strongly on the rheological properties of the material and the commensurate pressure required to extrude the material through the orifice. Here, we focus primarily on printing using conical nozzles with a 610-µm diameter at the outlet.

Mixing of particle-based viscoelastic fluids at these length scales is challenging. Moreover, because the final product is a transparent glass optic, the requirement for achieving good mixing is particularly rigorous to avoid scattering between microdomains of different refractive indices in the glass. Therefore, it is imperative that the inks are fully mixed as the filament exits the nozzle, which requires sufficiently long residence times in the micromixer. On the other hand, the mixer design must also provide a rapid response to changes in the programmed ink composition, which necessitates a shorter residence time. However, the latter requirement can also be accounted for by implementing strategic compensation of the dispense rates into the toolpath (39). Hence, the micromixer used in this work was optimized for longer residence time to ensure complete mixing within the filament. The design of this mixer has been described in detail and tested previously for mixing of reactive materials by Golobic et al. (38). Here, we simulate and validate the suitability of this mixer design for printing glass optics from viscoelastic nanoparticle inks.

The mixing quality of the printed structures was tested by computational fluid dynamics (CFD) simulations and validated experimentally using high-viscosity particle-based silica inks. The CFD simulations were performed for two identical inks at a mixing ratio of 1:1 and a range of rotational speeds of the mixer. The output was characterized by a coefficient of variation (COV) over the cross-sectional area of the nozzle outlet (37, 38). Experimentally, the quality of mixing was tested with fumed silica nanoparticle–based inks (34). Typically, visualization of mixing is carried out using a dye solution; however, in this case, a dye would not produce reliable results of particle mixing due to its high diffusivity. Instead, to provide contrast for optical imaging, one of the inks was doped with silica-coated gold nanoparticles. The gold core provided a detectable color change, while the silica shell of the particles ensured that the rheological properties of the ink remained unchanged (fig. S1), thus providing reliable information about mixing quality at the particle level. The results showed
good qualitative comparison between the CFD and experimental results and indicated that mixing speeds on the order of 100 rpm or greater were required for sufficient mixing of highly viscoelastic inks (Fig. 2).

3D printed GRIN optics based on conventional lenses
All GRIN glass optics were printed from ink formulations that we have previously reported (35, 36). These materials were shown to achieve optical quality and glass density on par with commercially available glasses (35). Compositional variation was introduced in the printing process by adjusting the relative mass flow rates of two inks with different titania dopant concentrations [as low as 0 weight % (wt %) and as high as 5 wt %] relative to the final glass composition while keeping the total mass flow rate fixed and using in-line active mixing. The printed green bodies containing composition gradients were thermally treated using a protocol similar to one previously described (fig. S2) (34). After the sintering process, the glass optics were polished flat. Samples were then analyzed using both electron microprobe, which measures the TiO2 and SiO2 concentrations in the surface layer, and phase-shifting diffraction interferometry (PSDI), which measures the optical path distance of light propagating through the bulk material.

We produced several GRIN optics at the ~1-cm scale (fully dense) based on conventional lenses, including a spherical, a cylindrical, and an aspheric lens (Fig. 3). The variation in glass composition across the lens results in a corresponding spatial change in refractive index, which enables these flat 3D printed components to perform the same optical functions as the equivalent conventional lens with surface curvature. The lens with a parabolic concentration profile shown in Fig. 3A (the equivalent of a conventional spherical lens) was 5× diffraction limited with a focal length of 145 cm. The Strehl ratio measured for this 3D printed GRIN lens was 0.27 (fig. S3). Lenses with Strehl ratio >0.8 are considered to have diffraction-limited performance. The cylindrical lens (Fig. 3B) focal line width was estimated at 100 μm with a focal length of 11 cm. The aspheric negative lens (Fig. 3C) had a 10× diffraction-limited focal spot with a focal length of ~61 cm.

Nonconventional refractive index profiles
In addition, we were able to produce unconventional refractive index gradients with nonmonotonic and sharp profile changes (Fig. 4). While these GRIN glass samples were not aimed at performing a particular optical function, they demonstrate the ability to create refractive index profiles that would be difficult or impossible to achieve using diffusion-based methods, which are typically limited to parabolic profiles. Hence, these GRIN glass optics can be thought of as steps along the path toward truly arbitrary, 3D refractive index profiles, which could markedly expand the design space for optical components with advanced functionalities.

GRIN glass characterization and performance
Measurements of the ultraviolet-visible transmission of the optics are provided in fig. S4. All components have average transmissions ranging from 74 to 98% at 400 to 850 nm. Below 400 nm, however,
there is greater variability in transmission due to composition-dependent differences in the transmission cutoff. The data are in line with previous results, which showed that 3D printed glass with lower TiO₂ had a band edge near 260 nm, while glass with 5% TiO₂ had a cutoff around 365 nm (35).

Although the starting sol-gel inks had mass concentrations of 1.5 and 5% TiO₂, the concentration profiles for the various optics were programmed to run between 10 and 90% by volume of the 5% TiO₂ ink, yielding printed concentrations ranging between 1.85 and 4.65% TiO₂. These values are in reasonable agreement with the TiO₂ concentration profiles measured by electron microprobe and shown in Figs. 3 and 4. On the basis of measurements using a prism refractometer (Metricon 2010/M) at 532 nm to characterize the index change of Figs. 3 and 4. On the basis of measurements using a prism refractometer (Metricon 2010/M) at 532 nm to characterize the index change of,

> \textbf{DISCUSSION}

Composition control in silica-based glass was achieved by room temperature, in-line blending of two silica-titania particle–loaded pastes of different titania concentrations using a DIW printer equipped with an active inline mixer. The compositionally varying green body was then thermally treated and consolidated to fully dense, transparent glass. The spatial variation in titania concentration imparted through printing is maintained during consolidation and yields a refractive index profile within the glass. Using this approach, near net-shape, transparent, silica-titania GRIN glass of 1 cm in extent was produced with an index change of up to 0.008 and a transmission above 74%. In addition to spherical and cylindrical GRIN lenses, nonmonotonic radial GRIN and asymmetric linear GRIN profiles were also produced—expanding the range of profiles that could be accessed when compared with either conventional melt- or diffusion-based GRIN glass processing. Optical functionality was directly confirmed through the bulk material using interferometry.

GRIN lenses with optical performance of increasing complexity require further refinement of the materials and process. Development of a variety of printable glass preform inks (40) is paramount to achieving greater refractive index changes and expanding the design space. Additional printing and toolpath optimization are needed to maximize mixing quality of the output composition while minimizing lag time in composition changeover associated with capacitance in the dispensing system. Coprocessing of multi-material green bodies can be challenging as untested dopant species are introduced into the formulations. Resulting glass compositions will require characterization and mapping of glass phase behavior to prevent unwanted phenomena such as crystallization or phase separation. Last, increasing green strength during the drying process is imperative for the prevention of cracking and enabling process scale-up to achieve larger optics.

Although the results provided here show 2D gradient index optics with flat surface figure on simple cylindrical forms, DIW printing with active mixing unlocks the possibility to control glass composition (for a change of optical or other material properties) in three dimensions in addition to modifying surface figure and 3D structure—perhaps enabling entirely new types of optics. This approach is expected to expand the capabilities of 3D printing technologies and to open the door to the preparation of previously undiscovered glass functional materials with potential applications in optics, sensing, packaging, and microfluidic systems.

> \textbf{MATERIALS AND METHODS}

\textbf{Reagents}

The following reagents were purchased and used without further purification: ethanol (EtOH) (Pharmco-AAPER, 200 Proof ACS/USP grade, ≥99.5%), concentrated ammonium hydroxide (NH₄OH) (Sigma-Aldrich, 28 wt % in H₂O, ≥99.99%), tetraethylorthosilicate (TEOS) (ATMI, ultrapure double distilled), titanium (IV) isopropoxide (TIP) (Sigma-Aldrich, ≥97%), titanium diisopropoxide bis(acetylacetonate) (TDBA) (Sigma-Aldrich, 75 wt % in isopropanol), deionized water, propylene carbonate (PC) (Sigma-Aldrich, anhydrous, 99.7%), tetraethylene glycol dimethyl ether (TG) (Sigma-Aldrich, ≥99.9%), polyethylene glycol 8000 (PEG 8K) (Fisher BioReagents, ≥99%), and CAB-O-SIL EH-5 fumed silica (Cabot).

\textbf{Sol-gel nanoparticle growth}

The silica sol was prepared by mixing 304 ml of EtOH, 3.0 ml of concentrated NH₄OH (28 wt % in H₂O), 14.48 ml of H₂O, and 70.2 ml of...
TEOS in a 500-ml round-bottom flask. The sol was then aged at ambient temperature for a minimum of 5 days. Silica-titania (SiO$_2$-TiO$_2$) sols were prepared by reacting TIP with the surface of the silica particle (silica sol). SiO$_2$-TiO$_2$ sol batches (1.5 and 5 wt %) were prepared by adding a 1.2 ml TIP/10 ml EtOH solution and 3.54 ml TIP/20 ml EtOH solution to a batch of silica sol. The SiO$_2$-TiO$_2$ sols were then heated at 55° ± 2°C with continuous stirring until the pH of the solution was neutral, typically 2 to 3 days. Any agglomerates were removed from the sols before solvent exchange by vacuum filtering using a Büchner funnel (Whatman filter paper, grade 6).

**Ink preparation**

The printable sol-gel inks were prepared by a one-pot solvent exchange method similar to that previously reported (35). The appropriate amounts of low vapor pressure ink solvents (21.0 g of PC and 18.5 g of TG) were added to the TiO$_2$-SiO$_2$ sols, and EtOH and H$_2$O were subsequently removed by rotary vacuum evaporation. The resulting inks were scraped from the flasks and then mixed using a planetary centrifugal mixer (Thinky USA) for 30 s at 2000 rpm. The next step is matching the solids between two fresh prepared inks. Typically, ~2 g of TiO$_2$-SiO$_2$ inks (1.5 and 5 wt % of TiO$_2$ relative to final glass composition) was transferred to aluminum cups and put in a 300°C furnace for 12 hours to evaluate the TiO$_2$-SiO$_2$ sols. After adjusting the solids with a 50/50 blend solution of PC/TG, 6 g of the 25% PEG solution (1.5 g PEG 8K + 4.5 g PC) was added to the inks and mixed for 2 min at 2000 rpm. The final inks have 26.5 ± 0.2 wt % SiO$_2$-TiO$_2$ solids, and they are stable on the order of 1 week in a sealed container. Inks containing fumed silica were prepared by mixing CAB-O-SIL EH-5 particles, TG, and TDBA in a planetary mixer, as described previously (36), typically as an undoped (0 wt % TiO$_2$) and doped silica ink (1.6 wt % TiO$_2$).

**Rheology measurements**

Rotational rheology measurements were performed on a TA Instruments DHR-1 rheometer with a stainless steel parallel plate setup. The diameter of the upper plate was 25 mm, and the geometry gap (sample thickness) was 500 μm. Ink viscosity was measured for shear rates ranging from 0.01 to 100 s$^{-1}$. To obtain the viscosity profile at higher shear rates that the ink experiences in the micromixer (>100 s$^{-1}$), a Malvern Rosand RH10 advanced capillary rheometer was used. The high shear rates were obtained by extruding the ink at speeds of 5 to 300 mm/s through dies of various diameters (250, 500, and 1000 μm) and measuring the pressure using a pressure transducer with a range up to 1500 psi.

**CFD simulations**

The unsteady flow field is modeled by solving the conservation of mass, momentum, and transport equations for the mass fractions of each ink, as described previously (37). The modeling adopts a continuum approximation, i.e., assuming that the particles in the ink are much smaller than the length scales of the micromixer geometry. Hence, particle-particle or particle-wall interactions are not explicitly modeled. The simulations were carried out for two fluids having the same viscosities. The non-Newtonian viscosity of the inks is modeled by curve fitting the experimentally measured data with the analytical and empirical expressions shown in fig. S1A. The unknown variables were computed using a finite-volume code solver (STAR-CCM+ v.12.06.011, Siemens) and the previously described hexahedral cell mesh and boundary conditions (37). The two inks enter the micromixer inlets at constant mass fractions of $q_1 = 1$ and $q_2 = 1$ at velocity magnitudes chosen to ensure a printing speed (outlet velocity) of 10 mm/s. The velocity profile is fully developed at a sufficient distance upstream of the rotating impeller. The simulations were carried out for impeller rotating speeds of $10^2$ to $10^3$ rpm. The distribution of the two inks at the nozzle outlet is visualized as shown in Fig. 2, and the corresponding COV is calculated as

$$COV = \frac{\sigma}{\bar{C}} = \frac{1}{N} \sum_{i=1}^{N} \sqrt{(C_i - \bar{C})^2}$$

where $C_i$ is the local ink concentration, $\bar{C}$ is the concentration assuming perfect mixing ($\bar{C} = 0.5$ for a 50/50 composition of two inks), and $N$ is the number of sample points in the cross section of the outlet.

Typically, visualization of mixing is carried out using a dye solution; however, in this case, a dye would not produce reliable results of particle mixing due to its high diffusivity. Instead, to provide contrast for optical imaging, the gold core provided a detectable color change, while the silica shell of the particles ensured that the rheological properties of the ink remained unchanged (fig. S1), thus providing reliable information about mixing quality on the particle level.

**Printing**

The prepared SiO$_2$ and SiO$_2$-TiO$_2$ inks were transferred into 30-ml syringe barrels (Nordson EFD) and centrifuged at 4500 rpm for 5 min to remove air bubbles. The syringes were then mounted onto a DIW system, where they were extruded using linear actuators (Parker). The inks were mixed in-line using a custom active mixing system [previously described by Golobic et al. (38)], where both inks were fed into a mixing chamber and blended with a rotating spindle at approximately 1500 rpm while being extruded through a 610-μm nozzle. The nozzle was held in a fixed position, while the material was deposited onto a silicone sheet, which was clamped to a three-axis motion positioning stage (Aerotech). Before each print, a calibration procedure was performed to quantify the flow characteristics of the system, which was then used to calculate the flow rates necessary to achieve a desired compositional profile for a given geometry, as described previously (39). Typical print speeds were 10 mm/s.

**Heat treatment**

After printing, parts were stored at room temperature for 3 days, after which they were released from the substrate. The parts were then heat treated according to the heating protocol shown in fig. S2. All heat treatments were done in air. Prints were then placed on top of a lintless wipe that was soaked with tetratame and covered with a Petri dish. The prints were ramped to 100°C at a rate of 3°C/hour, followed by a dwell of approximately 10 to 14 days to ensure complete solvent removal. After this, the prints were placed in an alumina crucible, and residual organic material was removed by dwelling at 300°C for 4 hours, 375°C for 2 hours, and 600°C for 4 hours with a ramp (0.5°C/min). Once the organic material was removed, the prints were sintered to full density at 1150°C for 2 hours, ramped at 1°C/min. The heat treatment protocol depends on the size of the printed green body. The drying process relies on diffusion of organic species out of the green body. Assuming the same ink formulation and thus the same porosity and species diffusivities, one can estimate that the required drying time will increase proportionally to the square of the smallest diffusivity path. As such, if an optic thickness
increases by three times, the anticipated drying time can be expected to increase by nine times under the same conditions.

**Polishing**
After consolidation, the optics were ground and polished to remove texture from print lines and to achieve surface microroughness <1 nm rms, typical for transmissive optics. The glass components were first ground on each side using a 320 Boron Carbide abrasive to remove remaining print-line texture. The parts were then polished on a conventional pad polisher using cerium oxide polishing slurry (either Rhodia 1663 or Hastellite PO) until the surfaces were flat to within one wave. The grinding and polishing removed ~300 nm each from the upper and lower surfaces. Note that the fully dense components are all on the order of 1 cm in the largest dimension with thickness ranging from 1 to 5 mm after polishing, depending on the optic.

**Glass composition characterization**
The analysis of glass composition was performed using a JEOL 8200 electron microprobe. The glass compositions were sampled at relative distances of 10 mm with a beam diameter of 5 μm. The concentrations of TiO₂ and SiO₂ were determined from the obtained x-ray intensities as described previously (36).

**Optical characterization**
The spatial variation of the refractive index of 3D printed GRIN optical parts was measured by making a map of the transmitted OPD between the part and a reference path in air using a PSDI—a custom-built instrument that operates at a wavelength 532 nm. The instrument has a spatial resolution that can be varied from 4 to 13 μm, with an aperture varying from 4 to 13 mm and an OPD resolution of a few nanometers. The OPD represents the sum of two contributions—the physical variation in thickness of the part and the part’s variation in thickness-averaged refractive index. Because the surfaces were polished flat to within one wave, this physical thickness variation made a negligible contribution to the OPD, and therefore, we calculated the thickness-averaged refractive index by dividing the measured OPD by the mechanically measured thickness.

For typical GRIN parts, which are several millimeters thick, measurements of thickness-averaged refractive index variation have a spatial resolution of about 10 μm and a precision of a few percent per million. In some cases, there are missing data points in the measured OPD map. These dropout areas were typically caused by cracks or other anomalies that refracted light out of the collecting aperture of the interferometer. The focal spot and focal length were determined by computer simulation using data collected by the PSDI system. Digital holography by optical wave propagation software was used to project the measured OPD and transmitted intensity data to any spatial plane downstream of the lens. The focal length was determined by selecting the plane where the computed focal spot was the tightest.

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Competing interests: A patent application has been filed by the Lawrence Livermore National Security LLC based on the concepts described here (U.S. patent application serial no. 16/212,525). The authors declare that they have no other competing interests.

Data and materials availability: All data needed to evaluate the conclusions in the paper are present in the paper and/or the Supplementary Materials. Additional data related to this paper may be requested from the authors.

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