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Sol-Gel Based Nanoparticles for 3D Printing of Optical Glass

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Abstract:

Additive manufacturing also known as 3D printing provides an innovative way to produce gradient index (GRIN) lens and other high-performance optics. Novel inks for direct ink write (DIW) 3D printed optical glass have been reported; however, the refractive index has never surpassed a value of 1.48. Here, we report a ternary formulation of core-shell SiO_2 nanoparticles coated with a TiO_2 shell and GeO_2 nanoparticles that can be used as a feedstock for DIW lenses. Printable titanium-germanium-silica inks were prepared from colloidal sol-gel feed stocks to produce shear-thinning inks for DIW. The inks were dried and sintered following an optimized heat treatment to remove organic material and produce a transparent and void-free monolith. Through this method, we found that these lenses are transparent at dopant concentrations of 7 mol% TiO_2 and 14 mol% GeO_2. With higher dopant concentrations of germanium and titanium, these lenses subsequently have a refractive index of 1.52. Moreover, these inks share the same viscoelastic properties as previous shear thinning DIW inks, allowing these inks to be 3D printed.

Introduction:

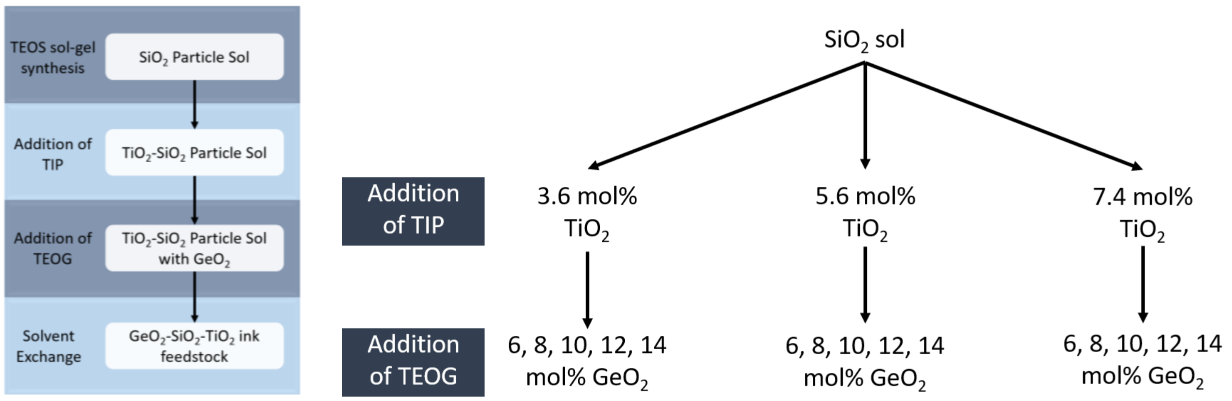
Glass is a desired material in optics as it has a high melting point and high transparency as well as optical properties to transmit, refract, and reflect light. For optics, the refractive index of the glass plays a critical role to produce these optical properties. Therefore, the ability to tune the refractive index of the glass is required to make advanced optical systems such as lasers or telescopic lens. At the atomic level, the refractive index of glass can be adjusted to a certain value based on the composition of oxides within the glass. For example, sodium oxide and titanium oxide can be added to the glass to increase the refractive index. However, the introduction of the different dopants into the glass create potential problems as they not only drastically change the optical properties of the glass, but also its thermodynamic stability and overall viability to form a transparent glass.

Additive Manufacturing or 3D printing provides a revolutionary approach to develop various assortment of materials ranging from biomaterials to resins. Although these methods have seen success in the production of other materials, a robust method to 3D print an optical lens has not been developed. For example, laser melting techniques appears to form transparent glass. However, bubbles resulting from differential heating can form within the glass. When the glass is furthered processed, the bubbles can cause a buildup of stress within the glass and lead to widespread cracking. Another method is a glass made through a UV curable ink and printed using photolithography to a form a full densified optical glass. However, the method has not shown yet to work with multiple component inks loaded with various dopants or been scaled up to print bulk materials.

In previous work, our group has reported a direct-ink write method- a novel approach to 3D printed lens. Unlike previous methods outlined above, fumed silica ink stocks are extruded through a thin nozzle to make a homogenous optical lens. Once printed, the ink solidifies through the gelation of silica structure. The parts are then thermally treated produce a crack-free transparent optical glass. However, the main challenge with fumed silica is an inconsistent mixture that affects all aspects of the glass. Fumed silica can agglomerate together and create domains of silica which are too large to be extruded. An unpredictable mixture also causes random defects that affects the lens' refractive index. To remedy these problems, feedstock use sol-gel based silica nanoparticles instead of fumed silica. Previous studies with silica and silica-titanium sol gel feedstock resulted in a colloidal suspension that can undergo direct ink write to produce an optical lens. Its transparency, refractive index, and coefficient of thermal expansion is comparable to a commercial lens.

One of the main objectives of developing lens through direct ink write is fabricating a lens with a desired refractive index. However, it can be a challenge to do so as the lens must also be crack-free, transparent, and printable. These factors must be in balance to make a successful optical glass. In this paper, the authors report the 3D printing of glasses made through a three-component mixture of germanium, silica, and titanium. Unlike the previous formulations of silica and silica-titanium inks, the ternary mixture enables better stability with germanium as a network former. Therefore, the overall concentration of dopants, in this case germanium oxide and titanium oxide, can increase the refractive index of the glasses without compromising its printability or transparency.

Results and Discussion



Ink Preparation- The preparation of GeO_2-SiO_2-TiO_2 consists of four main stages as shown in Figure 1. First, Germanium and Silica nanoparticles through the Stober process using Tetraethyl Orthosilicate (TEOS) as the Silica precursor and Germanium (IV) Ethoxide (TEOG) as the Germanium precursor. Water and ammonia catalyst are mixed together in an ethanol solvent and added to the precursors. Both the GeO_2 and SiO_2 particles grow to a mean radius of 18.5 nm within seven days, measured by dynamic light

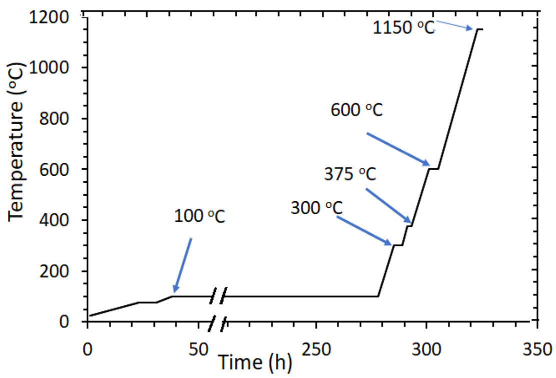
scattering (DLS). Titanium (IV) Isopropoxide (TIP) is then added to the SiO_2 and heated at temperature of 60°C for two days to form a core-shell SiO_2 nanoparticle coated with Titanium oxide. Overall, three sols of TiO_2-SiO_2 were formed with molar concentrations of 3.6%, 5.6%, and 7.4% TiO_2-SiO_2. From there, Germanium nanoparticles are added to a molar concentration of 6%, 8%, 10%, 12%, and 14% GeO_2-SiO_2.

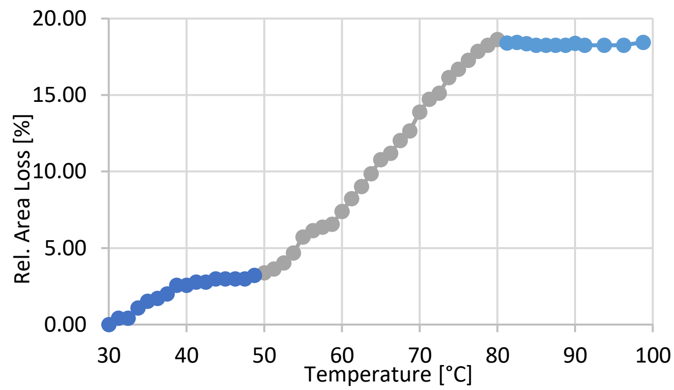
Desired Rheology- The GeO_2-SiO_2-TiO_2 sol undergo a solvent exchange to the tune rheology to a shear-thinning ink. Propylene Carbonate (PC) and Tetra ethylene Glycol Dimethyl Ether (TG) were chosen as solvents for their low vapor pressure and high elastic modulus. Upon extrusion, the printed glass held its shape. It is important to note the rheology must be adjusted to prepare a void-free monolith. This window of elasticity is small as a low viscosity will cause print lines and domains of silica to form. On other the hand, a high viscosity will cause the green body to slump. The rheology can be tuned by changing the ratio of Propylene Carbonate and Tetra Glycol Dimethyl Ether in the ink feedstock. By adding Propylene Carbonate into the solution, the repulsive force between the particles increased-dispersing the particles to form a more homogenous solution. A liquid with more Propylene Carbonate will ultimately lower the viscosity and the elastic modulus of the solution. Polycarbonate Carbonate behaves like a surfactant as it disperses the particles apart. On the other hand, the addition of Tetra Glycol Dimethyl Ether lowers the repulsive force between the particles. If a large amount of Tetra Glycol Dimethyl Ether is added into solution, the particles will agglomerate together and precipitate out of the solution as shown in figure two.

Predicting Rheology- Zeta potential predicts the like hood that the particles will agglomerate together. Since repulsive force is proportional to the slope of the electrostatic repulsive potential, zeta potential which measures electric potential at the slip plane can measure the repulsion between particles.

$$F_r = \frac{dV_R}{dh}$$

A high zeta potential will indicate that the particles are well dispersed in solution, while a low zeta potential mean that there is a higher attraction between particles. If the zeta potential is low enough, the particles can overcome any repulsion and coagulate together. It was experimentally found that particles in PC has a zeta of -20.04mV and particle in TG has a zeta of -2.65mV. This data numerically supports the observation that TG causes agglomeration as TG has a low zeta potential- indicating that





repulsion is reduce enough that the interface is attractive, and the particles are agglomerating. Compared to TG, particles are more stable in PC as these particles have a strong repulsion between each other.

Heat Treatment- Heat treatment is of interest as the glass undergo stresses caused from the additional heat. These stresses can accumulate and cause the formation of cracks throughout the body. To try to mitigate the formation of cracks, the green bodies undergo a three-step heat treatment to produce a three component GeO_2-SiO_2-TiO_2 glass. First, the green bodies are dried at 100°C for several hours to remove solvent and strengthen the structure. Then, the furnace is ramped to 600°C to completely decompose and remove all organic material within the structure. Finally, the green body becomes full densified at 1150°C.

The first step is important as majority of the mass loss occurs at this step. This loss has the potential to buildup stress and create cracks throughout the monolith. To measure the mass loss, a camera mounted above the furnace recorded monolith for the first step. Shown in figure three, three different shrinkage rates were observed between 30°C and 100°C. Between 30°C and 50°C, the glass shrink at a slow rate. After 50°C, the shrinkage occurs rapidly until 80°C. Finally, the shrinkage stops at 80°C. It is worth noting that a buildup of stress will occur after 80°C as additional capillary forces cannot be alleviated through shrinkage. From this point onward, the rate of heating must be carefully chosen to reduce the probability of cracking in the monolith.

Transparency-

Through this study, we developed a three-component feedstock for 3D printed GRIN lens with a higher refractive index. By varying the concentration of GeO_2 and TiO_2, we tested the viability of glass in terms of transparency and printability. The glass was transparent up to 7 mol% TiO_2 and 14 mol% GeO_2. Also, a higher colloidal stability of the glass could be seen through the zeta potential of the nanoparticles. While these glasses are not completely crack-free, a range of temperatures were identified as cause of cracking. Experiments to optimize ternary glass through the addition of surfactants and to reduce cracking during heat treatment are ongoing.