Direct ink writing of cellulose-plasticized aqueous ceramic slurry for YAG transparent ceramics

Haohao Ji, State Key Laboratory of High Performance Ceramics and Superfine Microstructure, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050, China; Center of Materials Science and Optoelectronics Engineering, University of Chinese Academy of Sciences, Beijing 100049, China; CAS Key Laboratory of Transparent Opto-functional Inorganic Materials, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 201899, China

Jin Zhao, State Key Laboratory of High Performance Ceramics and Superfine Microstructure, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050, China; CAS Key Laboratory of Transparent Opto-functional Inorganic Materials, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 201899, China

Jie Chen, School of Mechanical Engineering, Jiangnan University, Wuxi 214122, Jiangsu, China

Shunzo Shimai, Hetuo Chen, and Guohong Zhou, State Key Laboratory of High Performance Ceramics and Superfine Microstructure, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050, China; CAS Key Laboratory of Transparent Opto-functional Inorganic Materials, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 201899, China

Jian Zhang, and Shiwei Wang, State Key Laboratory of High Performance Ceramics and Superfine Microstructure, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050, China; CAS Key Laboratory of Transparent Opto-functional Inorganic Materials, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 201899, China

Dongliang Yang, Shandong Guiyuan Advanced Ceramics Co., Ltd., Zibo 255000, Shandong, China

Address all correspondence to Yu Liu at yuliu@jiangnan.edu.cn, Jian Zhang at jianzhang@mail.sic.ac.cn and Shiwei Wang at swwang51@mail.sic.ac.cn

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Abstract

Aqueous transparent ceramic YAG slurry with high solids loading up to 52 vol.% is proposed in this work for 3D direct ink writing. Celluloses are readily adjusted in the slurry design to enhance the plasticity, through which both printability of ceramic slurries and the optical quality of transparent ceramics are considerably improved. We demonstrate that the in-line transmittance at 1064 nm for a 1.2-mm-thick YAG ceramic can approach about 81.0%. This research provides a facile 3D printing routine for manufacturing transparent ceramic from water-based slurry.

Introduction

Transparent YAG ceramics are being developed for medicine, information, defense, environmental and scientific research fields[1,2] due to their excellent optical and thermomechanical properties. In recent years, the mold-less production of ceramics by additive manufacturing (AM) has attracted increased interests in advanced ceramics, since it allows for rapid fabrication of complex ceramic 3D structures with relatively fine features.[3-6] So far, there have been different AM techniques under consideration, such as stereolithography,[7-9] laser direct deposition,[10,11] and direct ink writing (DIW).[12-16] Wherein, DIW represents one most straightforward scheme for controlling the spatial distribution of the material ingredients, and therefore for the fabrication of multi-component and complex structured ceramic parts.[13,19]

For the DIW fabrication of transparent ceramics, there are rigorous requirements for tuning the rheological properties of the ceramic slurry. For example, the slurry should have good flowability for being extruded continuously and uniformly from the narrow nozzle. Upon extrusion, the slurry should rapidly develop a high enough yield strength to resist shape deformation or collapse.[17-19] Although, Jones et al.[13] and Zhang et al.[12] produced transparent ceramics by DIW using slurries, the ceramic slurries used so far only had a solids loading of less than 40 vol.% in that a significant amount of organics were necessary, limiting the further increase of the solids loading. Moreover, these organics will cause unexpected defects, i.e., cracks in green bodies during debinding. As a result, a low density of the green bodies can only be obtained, which hampers the possibility of getting a higher optical quality.[15]

Inspired by extrusion molding, we propose that ceramic slurries with plasticity are suitable for DIW process. The initial way to improve the plasticity of ceramic slurries is to add clay[20-22] or other additives. For the transparent ceramics, the introduction of impurity ions should be maximally avoided, and therefore the organic additives such as cellulose are more suitable to be considered[23-26] because that can be completely removed via heat treatment. Furthermore, the cellulose can effectively adjust the free water content in the slurry by forming hydrogen bonds with water molecules, which means it is highly hygroscopic.[27] Even more specifically, the contact between cellulose and water produces a rapid swelling in crystalline regions, as caused by the chemical adsorption of water in the amorphous region of cellulose and the physical adsorption of water by the pore structure. Besides, cellulose molecules are arranged in chains and can act as a lubricant between ceramic
particles, \cite{27} which reduces the friction between particles, as shown in Fig. 1(a). In conclusion, cellulose increases the plasticity of the slurry by reducing the free water content and lubricating effect, which plays a similar role to the clay.\cite{20–22}

In this work, transparent ceramic slurry with high solids loading was first prepared, then hydroxyethyl cellulose (HEC) was used to adjust the plasticity of the slurry to meet the needs of DIW. Their effects on the viscosity and the shape retention of the slurries were investigated. Also, the influences of the solids loading on the density of green bodies, grain size and optical properties of the ceramics were studied.

**Experimental Materials**

Commercial Al$_2$O$_3$ (99.99 wt% purity, Taimei Chemical Co., Ltd, Japan) and Y$_2$O$_3$ (99.99 wt% purity, Jiahua Advanced Material Resources Co., Ltd, Jiangyin, China) powders were weighed according to the stoichiometric ratio of Y$_3$Al$_5$O$_{12}$ (YAG). 0.1 wt% MgO and 0.5 wt% tetraethyl orthosilicate (TEOS, Sigma-Aldrich, 99.999%) were added as sintering additives. The powders were ball-milled in anhydrous ethanol for 12 h. The slurry was dried in oven for 24 h and sieved through an 80-mesh grid. The micromorphology of the raw material powders and the mixed powder are shown in Fig. 1(b). The particle size of alumina powder is quite different from that of yttrium oxide powder. It can be seen that the particle size of the yttrium oxide powder decreased after ball milling, and it can be uniformly mixed with the alumina powder. The sieved powder was heated at 2°C/min to 800°C and held there for 2 h to remove the organics. The calcined powder was then sieved once through an 80-mesh grid. CE-64\cite{28} (Dolapix CE-64, Zschimmer & Schwarz, Germany) was added as a dispersant, hydroxyethyl cellulose (denoted as HEC, Shanghai Macklin Biochemical Co., Ltd., 3400–5000 mPa·s, China) as a thickener, 0.5 wt% glycerol (Sinopharm Chemical Reagent Co., Ltd., China) as a lubricant. The addition of glycerol can effectively reduce the friction between the slurry and the needle. The surface of the slurry was smooth after extrusion, which was conducive to the bonding between the filaments. The dispersant and powder were added to the deionized water in sequence and ball-milled for 1 h. Cellulose and glycerol were added to the slurry.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1.png}
\caption{(a) Schematic diagram of cellulose swelling: (left) structure of cellulose before swelling, (center) thickening effect of cellulose swelling, (right) hydrogen bonding between cellulose chains after swelling, (b) SEM images of Al$_2$O$_3$ powder, Y$_2$O$_3$ powder and mixed powder, (c) The schematic diagram of the procedure for the preparation of transparent YAG ceramics by direct ink writing.}
\end{figure}
were added to the ball-milled slurry, which was then mixed uniformly and degassed by a vacuum mixer.

### 3D printing and sample preparation

After degassed, the prepared ceramic slurry was loaded into a syringe, and then printed on a glass substrate by a homemade DIW 3D printer, consisted of a three-axis gantry stage with a multi-axis motion controller. The linear positioning accuracy of the stage was ±5 μm with feedback resolution of 1 μm. All movements were programmed in C#. The printing speed was 3 mm/s, the inner diameter of the needle was 0.52 mm, the line spacing was 0.6 mm and the layer thickness was 0.35 mm. To control the drying process, the printed wet bodies were placed in a constant temperature and humidity chamber for drying. The dried green bodies were heated in a muffle furnace at 1°C/min to 800°C for debinding. Then the samples were vacuum sintered in a vacuum furnace at 1700°C for 6 h. The sintered samples were polished on both sides for in-line transmittance test. The preparation process was schematically presented in Fig. 1(c).

### Characterizations

The rheological properties of the slurry were characterized by a rotational rheometer (Haake Viscotester iQ Air, Thermo Electron GmbH, Germany), a flat plate with the diameter of 20 mm was selected, and the temperature of the test platform was controlled to be constant at 25°C. The density of the thermal treated green bodies and ceramics was measured according to the Archimedes principle. The average pore diameter and porosity of the thermal treated green bodies were tested with a mercury intrusion porosimetry (Poremaster60, Anton Paar, Austria). The fracture surface morphology of the green bodies and ceramics was observed by scanning electron microscope (FEI Magellan 400, FEI, USA). The polished surface of the ceramics was observed by scanning electron microscope (TM3000, Hitachi, Japan). The average grain size of the ceramics was estimated on the SEM micrograph by the linear intercept method. Mean grains size was estimated over at least 100 grains to ensure good measurement reliability. Each grain is approximately spherical, and the true average grain diameter \(G\) can be expressed as a function of the average apparent grain size \(g\) obtained from the SEM micrograph:

\[
G = \frac{\sqrt{6}}{2} g
\]

The in-line transmittance of polished ceramics with a thickness of 1.2 mm was measured by an ultraviolet–visible spectrophotometer (V-770, JASCO Corporation, Japan).

### Results and discussion

Figure 2(a) shows the effect of CE-64 content on the viscosity of the slurries with 50 vol.% solids loading. With the increase of CE-64 content, the viscosity of ceramic slurry shows a trend of first decreasing and then increasing. This can be explained that with the increase of dispersant content, the electrostatic repulsion between ceramic particles increases and the slurry viscosity decreases. When the content of dispersant is higher than an upper limit, the excess dispersant increases the ionic strength of the slurry, which compresses the electric double layer and reduces the electrostatic repulsion between particles. Thus, an optimal dispersant content of 0.6 wt% relative to the powder mass fraction has been found in our work.

In order to study the effect of the cellulose on the slurry, the viscosity before and after adding cellulose to different solids loading was compared, as shown in Fig. 2(b). The results show that for slurries with different solids loading, the viscosity increases by dozens or even hundreds of times after adding the celluloses. For example, the viscosity of 50 vol.% solids loading slurry without adding cellulose at 100 s\(^{-1}\) is only about 0.14 Pa·s, but the viscosity significantly increases up to 11.39 Pa·s just after adding about 0.5 wt% cellulose. When the solids loading of the slurry was 54 vol.%, shear thickening was observed after adding cellulose, and its viscosity was too high to be used for printing. The thickening effect of cellulose on the ceramic slurry is mainly achieved through swelling. [27,30]

On the one hand, hydrogen bonds are formed between cellulose and water molecules. The chemical adsorption of water in the amorphous region and the physical adsorption of water in the pore structure restrict the movement of free water in the slurry. On the other hand, cellulose increases in volume due to swelling, squeezing the ceramic particles to reduce the distance between them, thereby increasing the viscosity of the slurry.

The printability of the slurry after modified with cellulose has been significantly improved, as shown in Fig. 2(c). It can be seen that for the slurries with different solids loading, when the amount of cellulose as added was low, the slurries formed droplets after extrusion. The reason is that the flow point of the slurry is too low, as shown in Fig. 2(c) (i), (ii), (v), (vi) and (ix). However, after the pressure was unloaded, the slurry dropped under its own residual elastic force and gravity. Although the extruded slurry did not drip, as shown in (iii) and (x), the volume flow rate during extrusion was unstable, and the slurry still flowed after deposition due to the lack of shape retention. A slurry with a suitable amount of cellulose had a suitable flow point, good printability, and clear lines after extrusion, as shown in (iv), (vii), (viii) and (xi). However, cellulose, like other organic additives, is pyrolyzed during the debinding process and leaves pores in the green body, which will reduce its density and affect its densification during sintering. Therefore, under the premise of effectively improving the printability of the slurry, the amount of cellulose should be as low as possible. According to the above experimental results, in the subsequent ceramic preparation process, cellulose addition in the slurry with solids loading of 48 vol.%, 50 vol.%, and 52 vol.% was 0.50 wt%, 0.38 wt%, and 0.30 wt%, respectively. For the slurry with much higher cellulose addition, the bubbles in the slurry were difficult to be removed and the intermittent appearance of bubbles...
during extrusion caused defects on the green body, as shown in (xii). Defects in the green body will affect the microstructure of the ceramic, such as pores, which will seriously affect the optical quality.

Since the process of DIW is accumulation of ink printing layer by layer, it may leave printing marks (knit lines) unique to additive manufacturing in the green body, which is detrimental to the dense structure. The scanning electron microscope was used to observe the microstructure of the green body with different solids loading, as shown in Fig. 2(d). The results show that for the inks prepared with different solids loading slurries, the green bodies have a relatively complete and dense structure without obvious printing marks.

In order to study the influence of solids loading on the average pore size and porosity of the thermal treated green body, the mercury intrusion method was used to test it, shown in Fig. 3(a).
The results show that with the increase of solids loading of the slurry, the pores average size and porosity of the green body decrease. As the solids loading of the slurry increases from 48 to 52 vol.%, the porosity of the green body decreases from 0.150 to 0.135 cc/g. The increase in the solids loading of the slurry contributes to increasing the packing density of particles in the green body. The bulk density and relative theoretical density of thermal treated green bodies prepared from different solids loading slurries were measured. With the solids loading increases from 48 to 52 vol.%, the bulk density of the green body increases from 2.538 to 2.615 g/cm³. The relative density of the green body formed by direct ink writing can be up to about 57.5%, which is higher than that by cold isostatic pressing after dry pressing of the same powder (about 56.1%).

The influences of the ceramic microstructure on optical quality were studied. It can be seen from Fig. 3(c) (i–iii) that for the ceramics prepared from different solids loading slurries, all of them display the fracture features of intergranular fracture and the grain size is uniform. The results in Fig. 3 (c) (iv–ix) show that as the solids loading increases, the grain size of the ceramics increases. For example, with the solids loading increases from 48 to 52 vol.%, the grain size of the ceramic increases from 9.3 to 13.5 μm. The increase in solids loading of the slurry increases packing density of particles in the green body, so the densification rate and grain growth rate are faster at the same sintering temperature. However, a small number of pores were found in the ceramics prepared with 48 vol.% and 50 vol.% slurries, as shown in Fig. 3 (c) (vii) and (viii), while few pores were found in the 52 vol.% sample, as shown in Fig. 3(c) (ix). With the increase of solids loading, the packing density of ceramic particles is higher, which is more conducive to the densification process.

Transparent ceramics were obtained after vacuum sintering at 1700°C for 6 h. Figure 3(d) shows the in-line transmittance of ceramics (1.2 mm thick) prepared from different solids loading slurries after polishing. In-line transmittance of the ceramics slightly increases with the increase in solids loading from 48 to 52 vol.%. It falls in our expectation that the ceramic prepared from 52 vol.% solids loading slurry have the highest in-line transmittance of about 81.0% at the wavelength of 1064 nm, which is almost close to the theoretical transmittance of YAG ceramics. We also notice that the relatively lower

![Figure 3. Effect of slurry solids loading on the (a) average pore diameter and (b) porosity of the thermal treated green body, (c) SEM microstructure images of (i–iii) fractured surfaces, and (iv–ix) polished and thermal etched ceramics surfaces from different solids loading slurries (Under different magnification), (d) In-line transmittance of the 1.2-mm-thick polished YAG ceramics from different solids loading slurry.](image)

| Slurry system and preparation method used for DIW of YAG transparent ceramics. | Zhanget al.[12] | Jones et al.[13] | This work |
|---|---|---|---|
| Slurry system | Aqueous | Organic | Aqueous |
| Organic content (wt%) | 4–6 | 20–55 | 1.5 |
| Solids loading (vol.%) | 36 | 30–45 | 52 |
| Relative density of green body (%) | – | 45 | 57.5 |
| Cold isostatic pressing | × | √ | × |
| Hot isostatic pressing (HIP) | × | √ | × |
| In-line transmission at 1064 nm (%) | 70 (1.45 mm) | Optical scatter<3%/cm | 81.0 (1.2 mm) |
| Composition profile | Single | Dual | Single |

The bold is the advantage of this work in this regard.
transparency in the short wavelength region was ascribed to the small amount of residue pores shown in Fig. 3(c).

The present works of direct ink writing YAG transparent ceramics are compared from slurry system, solids loading, optical quality, etc., as shown in Table I. It can be seen that the use of slurry with high solids loading and low organic content can effectively increase the density of green bodies without cold isostatic pressing, thereby further improving the optical quality of the ceramics. However, the method applied in this work still has some problems compared to the previous studies. For example, the drying time is long and the spatial distribution of the compositions in the ceramics is simple, which will be investigated in the future work.

Conclusion

This work developed a facile method of designing cellulose-plasticized aqueous slurry for modifying the printability during DIW. First, CE-64 was selected as the dispersant to prepare a slurry with high solids loading and low viscosity. The introduction of HEC further provided the possibility of high solids loading in the slurry without negatively impacting the shearing flowability for ink printing. The increase in cellulose content improved the printability of the slurry. However, slurry with too much cellulose addition exhibited shear thickening and cannot be used for printing. Then, YAG ceramic slurries suitable for DIW were obtained. Our results demonstrate that ceramic green body with both high structural integrity and high relative density of 57.5% was successfully obtained, and 1.2 mm thick YAG ceramic had an in-line transmittance of 81.0% at 1064 nm.

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Data availability

Data can be available upon reasonable request to the corresponding author.

Declarations

Conflict of interest

The authors have no conflicts of interest to declare that are relevant to the content of this article.

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