CMT Ceramics in Modern Technologies
Techna Group srl



# Ceramic Additive Manufacturing Methods Applied to Sintered Glass Components with Novel Properties

Tassilo Moritz*, Jochen Schilm, Axel Rost, Eric Schwarzer, Steven Weingarten, Uwe Scheithauer, Katja Wätzig, Dörte Wagner, Alexander Michaelis
Fraunhofer Institute for Ceramic Technologies and Systems, Dresden, Germany

Additive Manufacturing methods offer groundbreaking new opportunities for geometrical complexity such as for personalization and individualization of ceramic components. Moreover, several AM processes suited for ceramic powders can also be applied to other materials like hard metals, metals or glasses. Two AM methods, one suspension-based (CerAM VPP – Ceramic Vat Photo Polymerization) and one feedstock-based (CerAM T3DP – Ceramic Thermoplastic 3D Printing) will be introduced in this article for making novel sintered glass components. The article will show results of process development as well as glass powder compositions with new functionalities.

*Keywords: Additive Manufacturing; Ceramic Components; Vat Photo Polymerization; Thermoplastic 3D-Printing; Sintered Glass Components.*

## 1. Introduction

### *1.1. Glass component production*

Glasses are mainly known for their optical properties. However, in addition to this, they may show a large variety of further advantageous properties like electrical conductivity, biocompatibility such as scratch, wear, and UV resistivity, or, in the case of silica glass, an excellent thermal shock resistance. Moreover, the possible color design of glass components embraces the complete color spectrum attainable either by pigments or by ionic colors [1, 2]. For that reason, glass components are of greatest interest for wide-spread applications like electronic components, micro reactors, biomedical components, filters, special heating elements or not at least for jewelry and design components. Most of the glass components today are made from a glassy melt by drawing, blowing, floating or pressing processes. However, for attaining components with sharp edges or any microstructure, for instance for micro channels in micro fluidic devices, the glass must be ground or etched by means of fluoric acid. On the other hand, simply shaped porous glass components, e.g. for filtering applications, may be attained by pressing of glass powders and subsequent sintering. Sintered glasses can obtain all properties known from conventional glass, but the perfection of optical properties. The reason for that can be seen in the residual pores remaining in the sintered glass structure after sintering and in possible crystallization and devitrification which may occur during sintering.
In comparison to sintering of ceramics, sintering of glass powders does not depend as much on diffusion processes, but from a viscous flow of the softening glass structure. This is the reason why sintering of glass is very sensitive to the sintering temperature and the holding time. Even exceeding the sintering temperature of about 5 K may cause a distortion of a glass component or a rounding of edges. [3-7] In recent development work [8] it could be shown that sintered glass components have been successfully manufactured by using powder injection molding technique. As known from ceramic powders, thermoplastic feedstocks had been prepared first, highly filled with different glass powders. Beside uncolored glass also different colored glasses have been used for making novel components, e.g. a watch case. Furthermore, it has been demonstrated in [8] that a certain electrical conductivity of sintered glass components can be attained just by adding a certain amount of graphite to the glass powder forming a percolation chain in the glassy matrix after sintering. Combining both, an electrical insulating and an electrical conductive sintered glass by 2-component injection molding allowed for producing a crucible or a nozzle with intrinsic heater as published in [9]. Despite the sintering process, the performance of the glass components was quite high with a density larger than 99% and mechanical properties comparable to glass parts produced from a melt.

### *1.2. Additive Manufacturing of ceramic and glass components*

Today, Additive Manufacturing (AM) methods offer a never known freedom in geometrical complexity due to a layer-wise, line-wise or dot-wise deposition of material basing on a CAD file. AM processes work cost effective, because no expensive tool is required, and AM methods are resource-saving, since material is only deposited where really needed for the desired components. Nevertheless, AM of ceramics and glass components is at a very early stage of development in contrast to AM of metal or polymeric parts. For ceramics this effect may be explained by the fact that AM processes remain powder processing as known from conventional ceramic shaping technologies, i.e. after the shaping process the ceramic part is still in the green state and needs to be debindered and sintered for attaining its final ceramic properties. This thermal post-processing comprises difficulties originating from the layer-wise construction of the ceramic parts.
AM processes for glass components either comprise a melt extrusion [10] limiting the shape of the glass components as

* *Corresponding author*
*E-mail address: tassilo.moritz@ikts.fraunhofer.de*

*https://doi.org/10.29272/cmt.2019.0008*
*Received January 8, 2019; Received in revised form February 20, 2019; Accepted March 7, 2019*

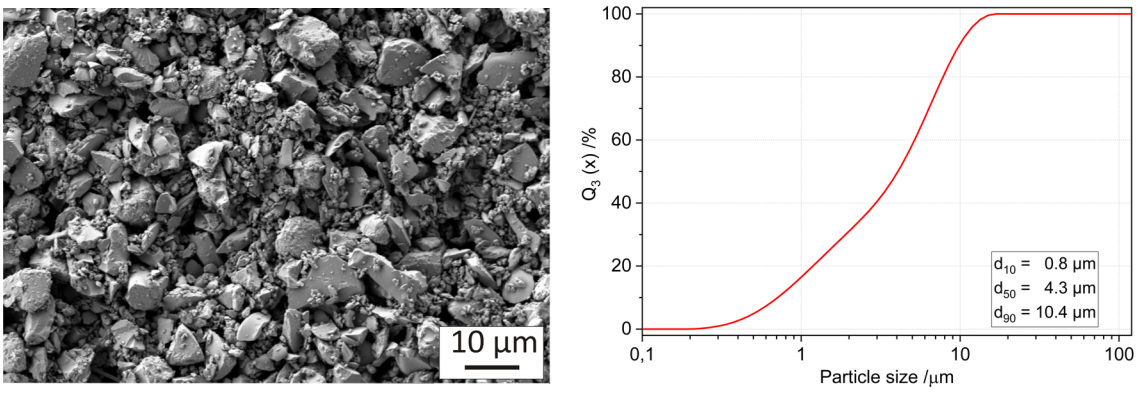
described for the conventional melt derived glass shaping technologies or stereolithography 3D printing of fused silica powders [11]. In the latter case a sintering is necessary as well.
When considering the state of the initial material for the building process, AM methods for ceramics can be differentiated into powder bed-based and suspension- or feedstock-based methods. The latter also include inks, slurries and pastes as initial materials. This simple classification in only two classes allows referring to a very important property of the initial materials defining the final properties of a ceramic component – the homogeneity of the particle distribution. The particle packing density in a powder bed-based AM process, like Binder Jetting (BJ) or Selective Laser Sintering (SLS), is commonly lower and much less homogeneous than the particle configuration in a suspension, in an ink or in a thermoplastic feedstock due to a much higher dispersion state of well-dispersed particles in a liquid or a molten thermoplastic binder. For that reason ceramic parts made by powder bed-based methods are hardly to densify to full density without any liquid phase during sintering. These components often contain a certain, occasionally desired porosity for applications like filters, catalyst supports or bone replacement parts. On the other hand, suspension- or feedstock-based AM methods in principle allow for attaining really densified ceramic parts with more than 99% of theoretical density.

## 2. Experimental

Being familiar with AM processes for ceramics is a door opener for applying these techniques to sintered glass components too. The authors dispose of five AM processes, two powder bed-based (Selective Laser Sintering, Binder Jetting), one suspension-based (Ceramic Vat Photo Polymerization – CerAM VPP), and two feedstock-based (Ceramic Fused Filament Fabrication – CerAM FFF, Ceramic Thermoplastic 3D-Printing – CerAM T3DP). Two of them, CerAM VPP and CerAM T3DP which are described here, have been used for development of sintered glass components.

### *2.1. Choice of glass powders and adjustment of novel glass properties*

Glass types that are suitable for the production of ready-to-use components for end users or as semi-finished products for integration into technical systems must exhibit high stability against environmental influences in order to prevent corrosion or leaching processes. Therefore, the use of explicitly low-melting glasses, such as those used for joining or sealing processes used in electronics, is not permissible. Such glasses usually suffer from insufficient chemical stability and decompose in contact with fluids. In order to meet the compromise between the lowest possible sintering temperature or softening temperature on the one hand and sufficient stability against environmental influences on the other, the glass type 8250 from Schott has been selected for the development of the additive shaping technologies. This highly insulating glass is widely used for the production of glass to metal feed through joints in combination with alloys like Kovar or with Molybdenum [12]. Hence with a value of $5{\cdot}10^{-6}$ $K^{-1}$ the coefficient of thermal expansion of 8250 matches well with these metals. The glass has been obtained directly from coarse granules and for the development of the feedstocks or slurries must first be processed into powders by grinding processes. In the first stage, the glass tubes were pre-crushed to a particle size of $< 500\ \mu m$ using a jaw crusher. In the second step, these coarse particles were ground down to a more suited particle size distribution in a jet mill ($d_{10} = 0.8\ \mu m$, $d_{50} = 4.3\ \mu m$; $d_{90} = 10\ \mu m$, $d_{99} = 14\ \mu m$). Figure 1a. shows the corresponding particle size distribution of the glass powder after this milling step and Figure 1b. a SEM image of the final powder. Unlike typical ceramic powders the glass particles usually have sharp edges and a spattered shape. Therefore, they can exhibit a highly abrasive behavior towards the linings of the machines during the preparation processes of feedstocks and slurries what in turn needs to be considered within the development processes.
With regard to the sintering processes, the viscosity of the 8250 glass is of decisive interest. Schott specifies for this glass a transition temperature Tg of 500 °C which corresponds to a viscosity of $10^{13}$ Pas. According to [13] glass powder compacts typically sinter in the viscosity range between $10^9$ Pas and $10^7$ Pas. When the viscosity reaches approximately $10^6$ Pas, the deformation of the sintered compacts already begins, resulting in a loss of shape accuracy and edge rounding. In order to evaluate these relevant temperature ranges the sintering and softening behavior of the glass powder has been investigated by hot stage microscopy according to the procedure described in [13]. A cylindrical powder compact (2 mm x 2 mm) is placed on an $Al_2O_3$-substrate and heated in steady air up to 1100 °C with 10 K/min while images are taken each 2 K. In Figure 2 the linear shrinkage of a 8250 glass powder compact is plotted against the temperature. The characteristic changes in the shape of the sample are depicted at along with the plotted data. At a temperature of 570 °C the sintering process starts indicated by a first shrinkage. At 696 °C the maximum shrinkage without a deformation of the edges is achieved. When a temperature of 730 °C is exceeded, a significant deformation of the edge can be observed what indicates a loss of the initial contour accuracy. These results give a temperature window of around 150 °C for the sintering process and the maximum temperature for sintered components is limited to 720 °C.
The characterization of the principal sintering behavior of the glass powder was done by using the pure glass powder without any additives. Powder compacts with a diameter of 8 mm and a height of approximately 10 mm were cold uniaxially pressed by applying a maximum pressure of 250 MPa. The powder compacts




*a.* *b.*

*Figure 1. SEM image of the 8250-glass powder after milling in jet mill (a) and corresponding particle size distribution (b).*

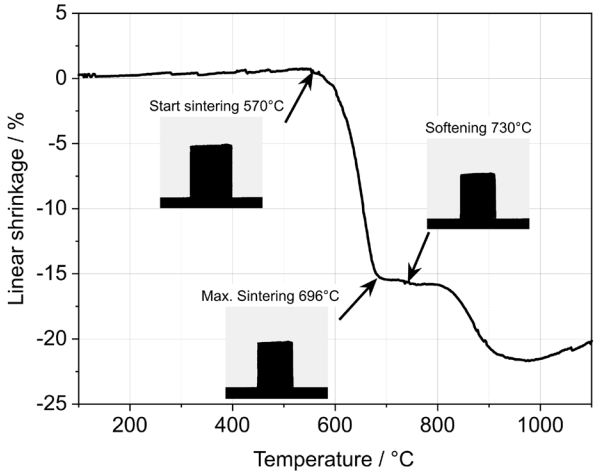
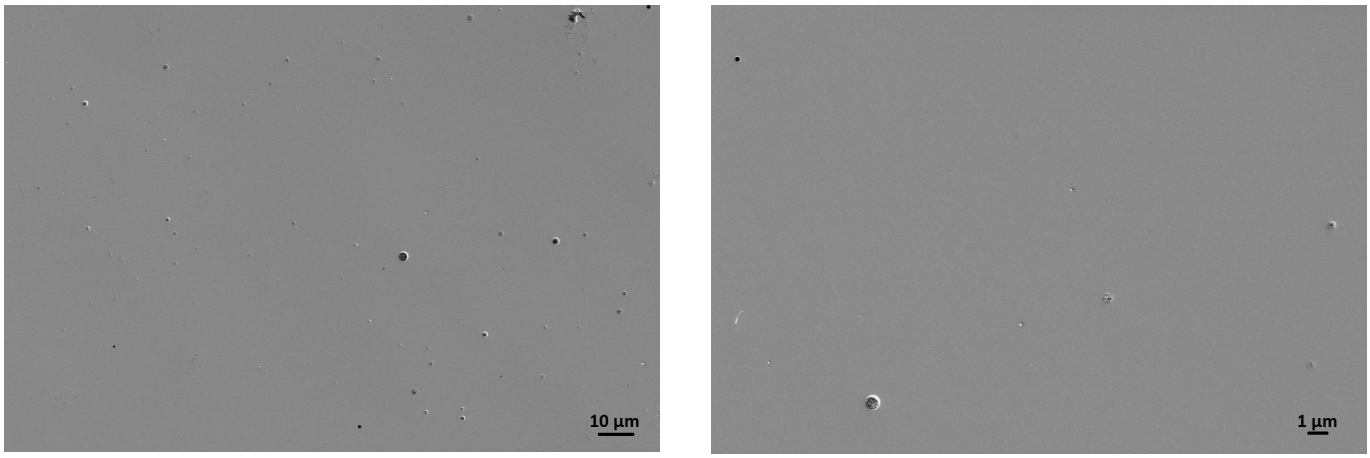



*Figure 2. Sintering behavior of a type 8250 glass powder compact analyzed by hot stage microscopy.*

The afterglow emission behavior has been analyzed for the green power compacts as well as for the sintered powder compacts. The comparison between the emission intensity of the non sintered powder compacts and the sintered samples at the detection wavelength of 520 nm with their percentage of the fluorescent component in the powder mixture is plotted in Figure 5. Up to a fraction of 40 wt.-% of the fluorescent component the afterglow intensity of the green powder compacts is lower than of the sintered compacts. We assume that this effect is caused by multiple internal reflections on the powder surface in the non sintered micro structure (Glass – Atmosphere – Fluorescent). In a dense sintered microstructure only interfaces between the glass and the fluorescent are existent. With an increasing content of the fluorescent component in the mixture this effects seems to be less effective. However the good correspondence between the green bodies and the sintered specimens indicates that the sintering step of the powder mixtures up to 700 °C seems not to affect the conversion behavior of the phosphor in a significant manner.




*a.* *b.*

*Figure 3. FESEM image of the micro structure of a sintered 8250 glass powder compact with different magnifications (a and b).*

have been sintered in air on a platinum substrate according to the following parameters: 20 °C – 5 K/min → 710 °C/10 min. Density measurements done by hydrostatic weighing showed that more than 99% of the theoretical density of the 8250 glass can be achieved with the sintering process. This result is confirmed by an inspection of the cross section of the sintered glass microstructure showing only a few circular pores and no grain boundaries (Figures 3a/b).

A major advantage in the processing of glass using the powder route is the possibility of realizing additional functionalizing by integrating particles. Within this article this ability will be demonstrated by the integration of ceramic fluorescent particles in sintered glass structures. For the tests the commercial alkaline earth aluminate long after glow phosphor powder HMK63D/L-L1 with a mean particle size of 28 µm was used. This material has a yellow-green emission color with an emission peak at 520 nm [14]. In a set of experiments, powder mixtures of the phosphor and the 8250 glass powder were prepared in graduated proportions of phosphor between 5 and 50 wt-% in a planetary ball mill. The powder mixtures were used to produce uniaxially cold pressed powder compacts. The afterglow behavior of the powder mixtures has been analyzed by UV/VIS spectrometry in the reflection mode. For the purpose of illustration Figure 4 shows the excitation spectra (dotted lines) with a peak maximum at 330 nm and the detected emission spectra (full lines) with a peak maximum at 520 nm measured at the sintered compacts. From the plotted data it can be seen that even a content of 5 wt.-% of the phosphor is sufficient to achieve a detectable afterglow effect.

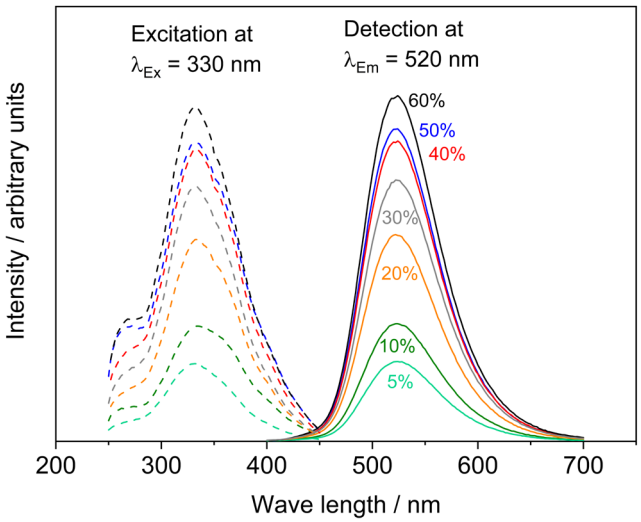



*Figure 4. UV/VIS-Spectra focusing on the excitation peak at 330 nm and the detection peak at 520 nm of 8250-HMK63D/L-L1 mixtures with different contents of the fluorescent component before and after sintering.*

### 2.2. CerAM VPP of sintered glass components

CerAM VPP or also known as Lithography-based Ceramic Manufacturing (LCM) as the first commercialized AM method

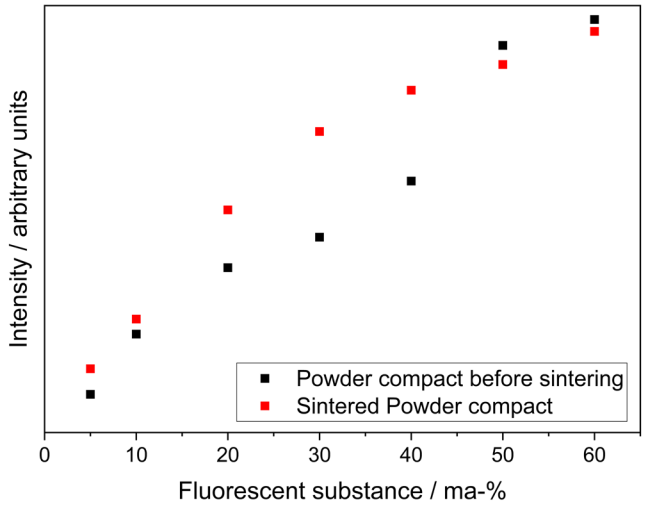



*Figure 5. Comparison of the emission intensity at 520nm of the powder compacts before (green) and after sintering.*

for making completely dense ceramic components bases on photo polymerization of light-curable monomers under exposure to a certain wavelength. Together with dispersing agents and photoinitiators the ceramic or glass powders are dispersed in the monomeric solution. Basically, the light-curable binder system consists of a combination of different monomers. For this, usually a long chain base monomer of higher viscosity is mixed with crosslinking monomers of higher functionality. In this publication a CeraFab 7500 (Lithoz, Austria) has been used. The component is built up layer-wise, hanging top down from the building platform. A new layer is applied by rotating of a vat containing a certain amount of suspension below a fixed doctor blade adjusting the layer thickness. Afterwards the building platform dives into the suspension layer and the layer is cured by light exposure from a DLP module situated beneath the transparent vat. Now, the building platform is lifted smoothly from the vat which rotates again for applying the next suspension layer. Uncured suspension flows back into the vat and is reused for the next layer. Using CerAM VPP requires an initial powder with a certain translucency for the wavelength which is applied for curing. This excludes materials with high absorption coefficients or opaque powders. Nevertheless, CerAM VPP today offers the highest surface quality and the best resolution in ceramic AM compared to all other AM processes. After the building process the component is removed from the building platform and cleaned. During the cleaning process uncured suspension sticking to the part's surface must be removed thoroughly for ensuring tight tolerances of the components. The production of high-quality and dense (> 99%) glass components by using lithography-based additive manufacturing technologies like the CerAM VPP process requires the development of a special photo reactive suspensions curable at wavelengths of approx. 452-465 nm. These suspensions should have a defined flow and curing behavior, advantageously comparable to commercial available suspensions, to adjust the printing process parameters of the CerAM VPP process easily for them. By tailoring the reactive binder system, new glass based suspensions were developed with the goal to maximize the sinter density and accuracy of printed components. In order to obtain a photo reactive suspension with a solid content as high as possible and at the same time high homogeneity combined with a certain flow behavior, a basic binder system based on acrylates was used. Thus, in all cases the binder system of the photosensitive glass suspensions were composed of a crosslinking system comprising at least two multifunctional acrylates to build up the polymer matrix, a mono-functional binder to act as a reactive diluent, a photo-initiator to start the polymerization upon exposure to blue light and a plasticiser for flexible green parts as well as easier debinding. In this study a suspension with a solid content of approx. 49 vol.-% based on the described 8250 glass was developed. In general, the developed binder system was a mixture of a monomer acrylate and two different multifunctional crosslinkers – a difunctional acrylate and a tetra-functional polyol acrylate. With an amount of 1 wt.% related to the photoreactive organic, camphorquinone as type II initiator was used. Additionally, a long chain polyethylenglycol was added as plasticizer.

The components were mixed and the suspension was prepared by using a high speed planetary ball mill (Thinky ARV 310, C3-Prozesstechnik, Germany). The homogenization and a degassing step (30 mbar) of the mixture were carried out in three steps: (i) 4 min at 1000 rpm, (ii) 45 s at 1500 rpm and (iii)30 s at 2000 rpm. After preparation, the suspensions were characterized to estimate a possible process setting for the CerAM VPP process.

The rheological behavior as well as the curing behavior are important characteristic values which can be used to determine optimal CerAM VPP parameters like curing time and process duration. Both properties were measured using a modular compact rheometer MCR302 (Anton Paar, Graz, Austria). The dynamic viscosity was measured at shear rates in a range of 0.01 to 1000 $s^{-1}$ at a temperature of 20 °C using a cone/plate measuring system (25 mm diameter). The curing behavior was analysed by oscillating measurements of the storage modulus G´ – a part of the complex shear modulus G* – before, during and after blue light exposure. Therefore, a plate-plate (glass) measuring system (diameter 25 mm) with a gap of 50 $\mu$m was used in combination with a blue LED light source (wavelength 452 nm, UV-LED Smart, Opsytec Dr. Gröbel, Germany). After suspension development different test samples, e.g. cubes, bending bars and a variety of geometric demonstrators were printed by using the CerAM VPP technology. The cleaned parts had been thermally debindered and sintered as necessary for the concerned material.

### *2.3. CerAM T3DP of sintered glass components*

This AM process uses a thermoplastic feedstock which composition bases on different waxes, like paraffin and beeswax [15]. Additives such as dispersants are used to stabilize the particles in the organic matrix. The proportion of organic ingredients is between 55 and 64 vol.-%. Thus, the viscosity of the feedstock is relatively low, shows a shear-thinning behavior and can be processed already at approx. 100 °C. Typical solid contents of CerAM T3DP suspensions are 36 to 45 vol.-%. The powder particle diameter may differ between a typical submicron powder and up to 5 microns. A rheometer (Modular Compact Rheometer MCR 302; Anton Paar, Graz, Austria) adjustable between -25 to 200 °C with a plate/plate measuring system was used to characterize the rheological behavior of the thermoplastic glass powder suspensions. The flow behavior was analysed with an increasing shear rate (0–1000 s-1) and at a temperature of 100 °C. The torque was measured and the dynamic viscosity was calculated. The high shear rates were necessary since the assessment of the conditions within the used micro dispensing systems, i.e. geometry of piston and nozzle chamber, velocity of piston revealed that shear rates of 1000 $s^{-1}$ and higher are generated in the micro dispensing system during the deposition process.

In this AM process the components are built up drop-wise by means of a micro-dispensing unit (VERMES, Germany) which works on the drop-on-demand principle. The nozzle orifice diameter is 100, 160, 200 or 300 microns, optionally, and the deposition frequency applied for the thermoplastic ceramic suspensions is 80 to 120 Hz.

Figure 6 shows a CAD-drawing of the used CerAM-T3DP-device with three micro dispensing units.

Depending on the solid loading, the viscosity, the surface tension and the wetting behavior of the suspension droplets with

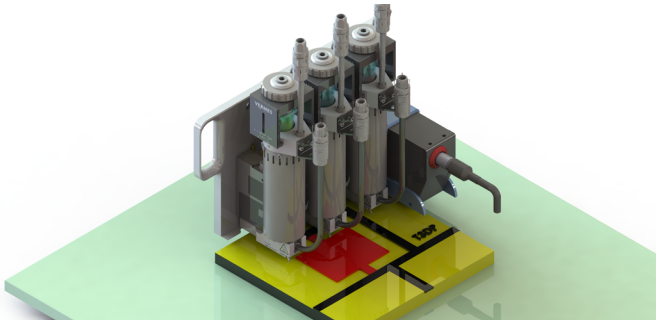


*Figure 6. CAD-drawing of the used CerAM-T3DP-device with three micro dispensing units.*

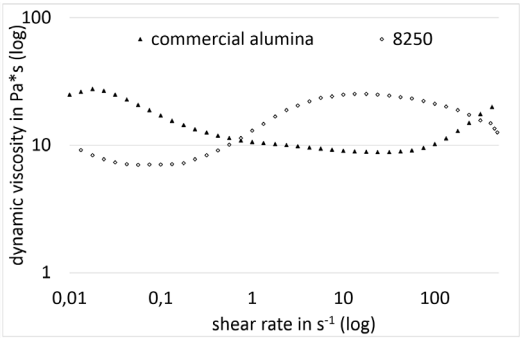



*Figure 7. Comparison of flow behavior by plotting the dynamic viscosity against shear rate for a 8250-suspension (glass content 49 vol.-%) compared to a commercial alumina suspension (Lithalox D350, high alumina purity, solid content approx. 50 vol.-%).*

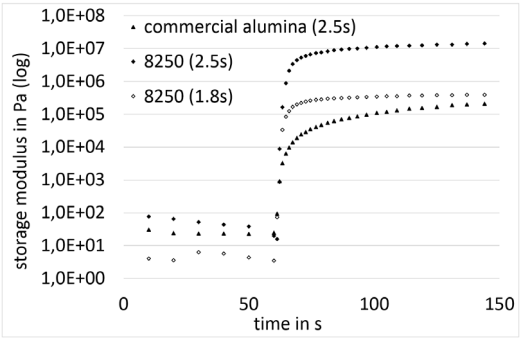



*Figure 8. Storage modulus against time of a 8250 suspension compared to a commercial alumina suspension.*

diameters between 250 to 350 microns can be deposited. By adjusting the distance between the single droplets overlapping occurs and line structures are attained. In contrast to ink-jetting, the deposited droplets do not dry – they solidify by cooling and the built components must be debindered afterwards. Starting with a new suspension, appropriate dispensing parameters have to be investigated [16]. For all deposited droplets, the droplet diameter, the droplet height, the roundness, and the volume are determined. Then the distance between the droplets is reduced, to form filament-like structures by fusing of adjacent droplets. For these structures the width and height are determined too. The correlation between the dispensing parameters and the properties of the generated droplets and structures allow the deduction of appropriate parameters for each suspension. Mixing and homogenization of the thermoplastic suspensions takes place in high-speed mixers like Dispermat CA-20C (VMA Getzmann GmbH, Germany) or, for larger badges, in heated ball mills. Debindering is carried out in a powder bed which is necessary for soaking up the liquefied binder coming out of the parts during heating up the debindering furnace. After that, the components are sintered as common for ceramics or, in this case, for sintered glass. Advantageously, depending on the number of micro-dispensing units one, two or more different suspensions may be deposited by this technique. Thus, either multi component parts can be built or supporting structure made of pure thermoplastic binder may be added which can be easily removed during the debinding step.

## 3. Results and Discussion

### *3.1. Glass components made by CerAM VPP*

The dynamic viscosity as a characteristic of the rheological behavior as well as the curing behavior are two important properties for the printing process and the quality of the printed components. The higher the slurry viscosity, the more likely parts will have quality issues. In contrast, if the viscosity is too low, it would be difficult or even impossible to print the suspension in a controllable and consistent manner due to the wetting properties of the fluid to the rotating vat of the CERAM VPP device. Varying the suspension's composition, the rheological and curing behavior can be adjusted.

In Fig. 7, the dynamic viscosity of the suspension containing glass powder is presented as a function of shear rate compared to a commercial alumina suspension. The level of the dynamic viscosity of the glass suspensions is generally comparable with a commercial alumina suspension, but the starting viscosity of 10 Pa*s is five times lower as compared to 50 Pa*s (commercial alumina suspension). However, the characteristic flow behavior is different. On the one hand, the commercial suspension shows a shear thinning behavior up to a shear rate of approx. 100 $s^{-1}$, and then a change to shear thickening occurs marked by an increase of the dynamic viscosity. On the other hand, the glass suspension also shows a shear thinning behavior, but only for shear rates lower than approx. 1 $s^{-1}$. At shear rates higher than 1 $s^{-1}$ up to approx. 50 $s^{-1}$ for the glass 8250 suspension, the trend changes to shear thickening behavior marked by an increase of the dynamic viscosity. After this, a shear thinning occurs again. An explanation for this behavior could be found in the shape of the ceramic glass powder particles. Compared to ceramic powders, the glass powder particles have sharp edges and a spattered shape (Fig. 1). Due to this, the shear thinning behavior predominates at low shear rates. But at higher shear rate, for this suspension > 0.1 $s^{-1}$, this behavior changes to shear thickening because the glass particles interlock caused by the movement. Only with higher shear rates (> 50 $s^{-1}$), the forces are high enough to break the interlocks and the viscosity reduces again. Using the glass suspension for printing, the applied shear rates should be lower than 1 $s^{-1}$ or higher than 10 $s^{-1}$, means very low or very high vat rotation. These results were used to adjust the setting of the CerAM-VPP process, especially the rotation of the vat by using a lower rotation speed in comparison to the commercial suspension.

The characterization of the curing behavior helps to estimate the curing time as an important printing parameter, which has to be adjusted in the CerAM-VPP process in dependence to suspension properties. In Fig. 8, the curing behavior for the 8250 glass suspension is exemplarily presented in comparison to a commercial alumina suspension by plotting the storage modulus vs. time.

During the characterization, the storage modulus of the suspensions before, during and after blue light exposure was measured. The exposure of the suspensions started at 60 s for a defined time with an intensity of approx. 33 mW/$cm^2$ comparable to the CerAM VPP process. The uncured glass suspensions show a low storage modulus of 10 to 50 Pa comparable to the commercial alumina suspension. As a result of the light exposure,

the storage modulus increased in dependence to the suspension and the curing time. By curing the commercial suspension for 2.5 s, a value which is used for rough designs in the CerAM VPP process for the commercial suspension, an increase of the storage modulus to approx. $10^5$ Pa was observed whereas the values for the 8250 suspension increase to a significantly higher value of approx. $10^7$ Pa. This can be interpreted as an indication for over exposure, because the commercial suspension reached similar values for longer exposure times. As a result, the exposure time for the glass suspension was reduced to 1.8 s (70% compared to the commercial suspension) leading to a reduced storage modulus. Accordingly, this exposure time was adjusted for the glass suspension in the CerAM VPP process for making glass components.

After suspension development and evaluation of CerAM VPP process parameters different test samples like cubes, bending bars,

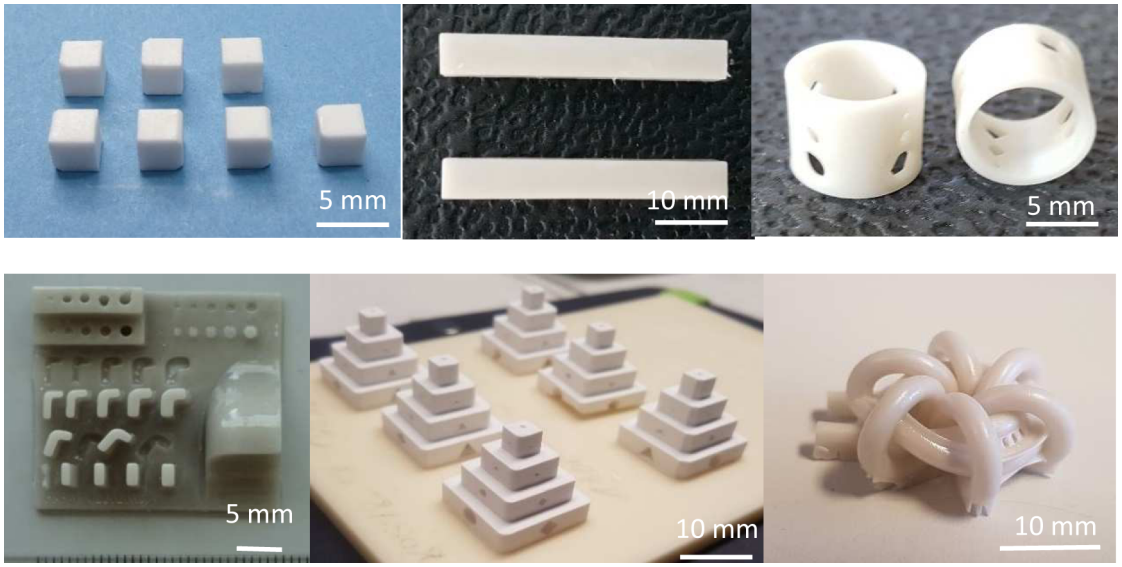



*Figure 9. Testing parts made of glass 8250 by CerAM VPP.*

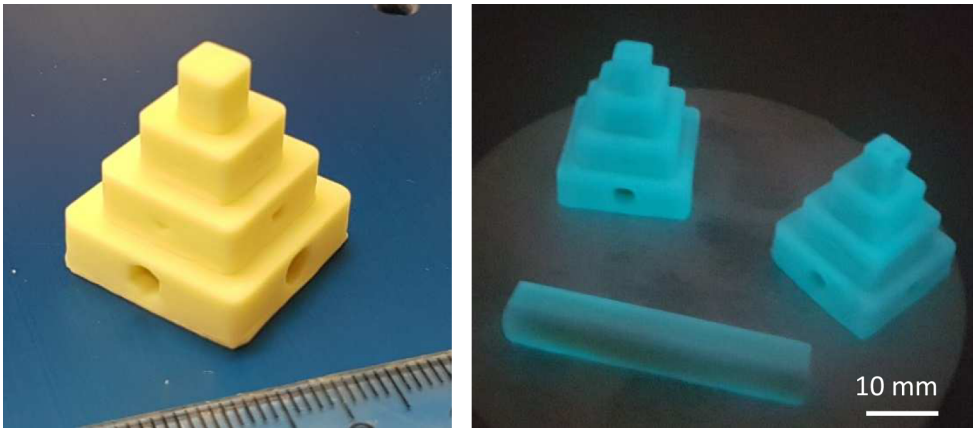
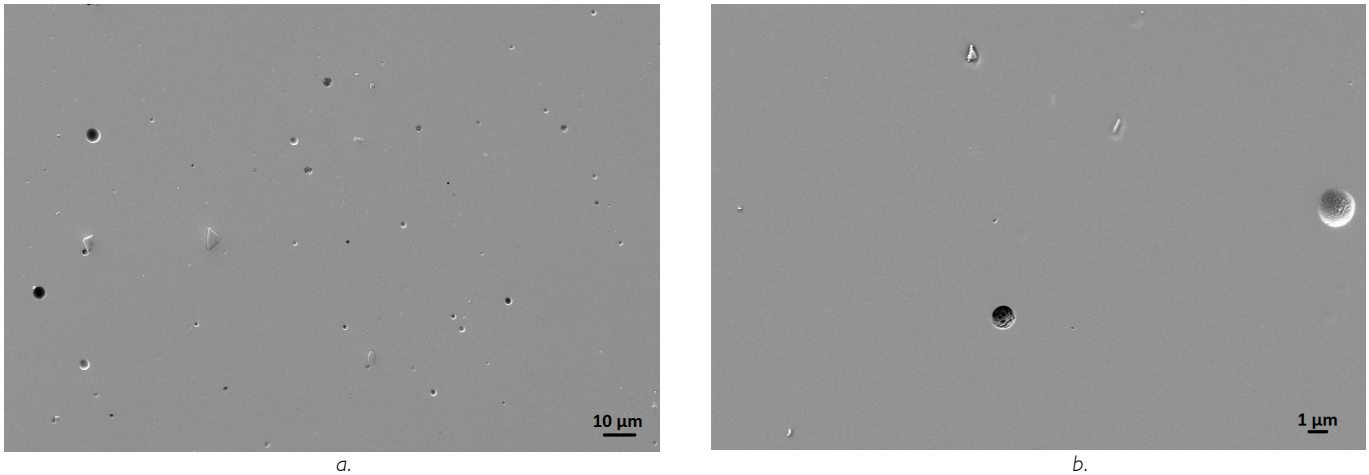



*Figure 10. Pyramidal test component with luminescent properties (left) made by CerAM VPP process and with blue luminescence visible in the dark (right).*




*a.* *b.*

*Figure 11. a/b FESEM images of sintered glass 8250 made by CerAM VPP with different magnifications.*

tubes and a variety of more complex geometry demonstrators were printed. The results are shown in Fig. 9.
In general, printing of different test samples by using the developed suspensions was successful as well as the thermal processing. The edges of the samples are sharp, quality of the components and the accuracy are acceptable. Sporadically, cracks or defects occurred, especially in the larger components as a result of a too fast thermal processing. Furthermore, some parts show deformations after sintering as a result of friction with the sintering support during sintering.

the fundament of the CerAM T3DP method. The low viscosity at higher shear rates allows for a dropwise dosing of the feedstock at the building platform and the steep increase of the viscosity after shut-off of the shear rate in conjunction with a fast solidification of the wax binder guarantees a certain mechanical stability of a chain of micro droplets against bleeding.
After the empirical determination of the dosing parameters the manufacturing of single component three dimensional structures became manageable. Figure 13 shows two sintered test structures basing on the glass suspensions additively manufactured by

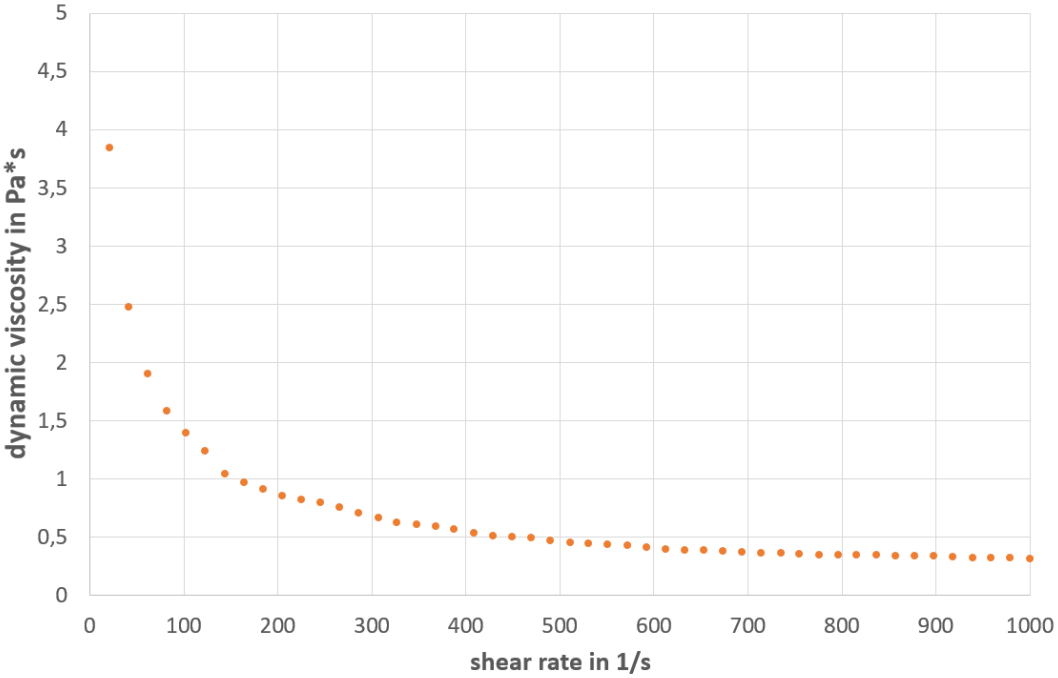



*Figure 12. Dynamic viscosity of a thermoplastic glass powder suspension vs. the shear rate.*

A further approach was to realize complex glass components with luminescent properties also by using the CerAM VPP technology. Therefore, the glass suspensions were adjusted by replacing 15 vol. % of the glass powder by a special luminescent pigment material. For example, in Fig. 10 a test component with a pyramidal geometry including a luminescent pigment for blue color is presented.
After thermal processing the sinter density of the printed test samples and demonstration components were characterized by hydrostatic weighing and the microstructure was analyzed by FESEM. The average of the measured sinter densities was higher than 99% as compared to the theoretical density of 2.28 g/cm$^3$.
In Fig. 11 a/b FESEM images of a sintered 8250 glass made by CerAM VPP are exemplarily presented in different magnifications. The microstructure shows a high homogeneity without any delaminations, cracks or other defects. Nevertheless, pores smaller than 5 $\mu$m were found, but they were randomly distributed within the micro structure. These pores can be a result of an inadequate degassing step during suspension preparation, which seems too short at 15 min duration. Such pores shall be avoided in the future by increasing the degassing time.

### *3.2. Glass components made by CerAM T3DP*

Fig. 12 shows the shear thinning behavior of a thermoplastic glass powder suspension with a solid content of 45 vol.-%. This rheological behavior is quite comparable to a low-pressure injection molding feedstock which isdescribed in detail by Novak et al. in [17]. The rheological properties of such suspensions form

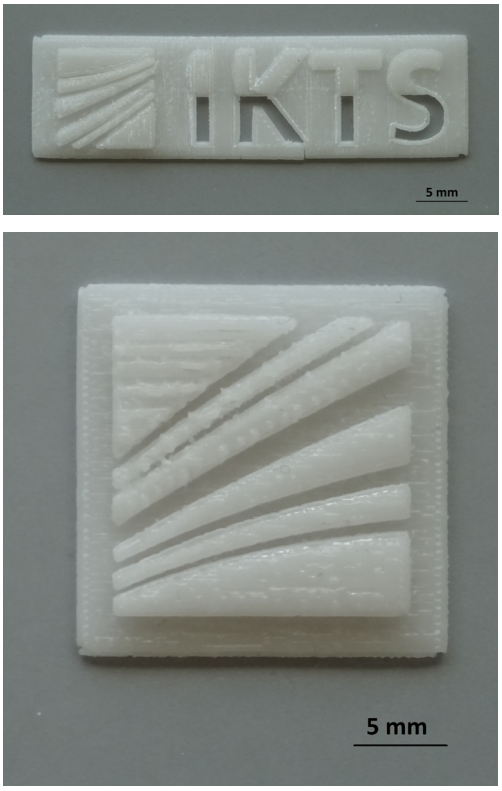
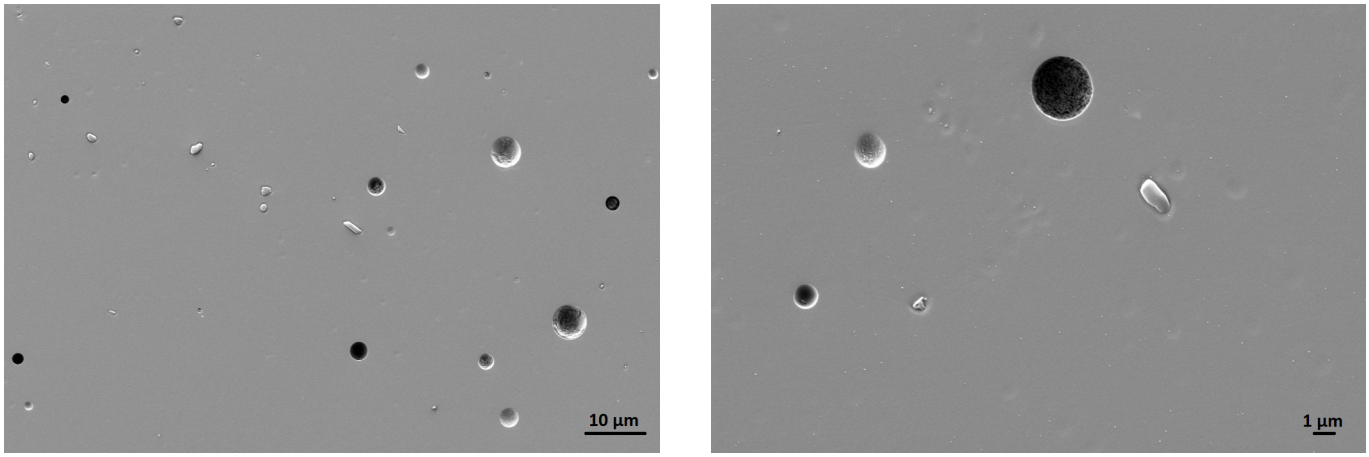



*Figure 13. Glass testing structures made by CerAM-T3DP.*




a. b.

*Figure 14. a/b FESEM analyses of the micro structure of a T3DP manufactured 8250 glass component in different magnifications.*

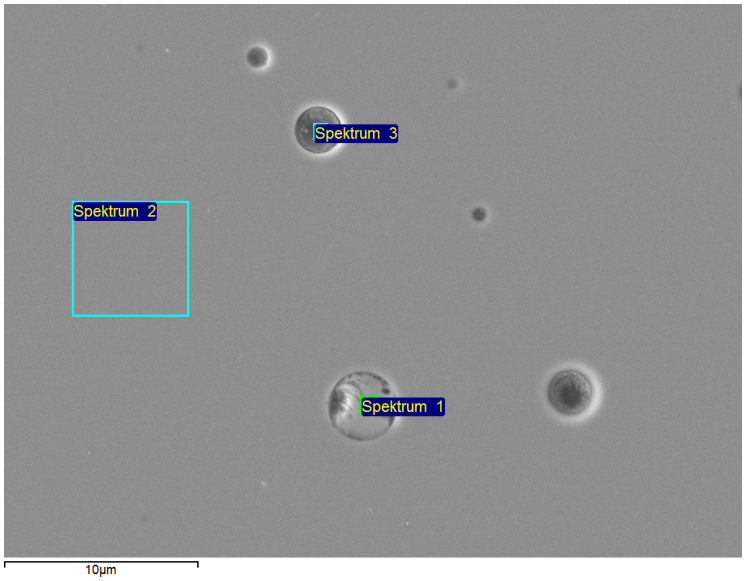



*Figure 15. FESEM image with marked areas of EDX analysis.*

CerAM T3DP.

FESEM images of the sintered samples were utilized to evaluate the samples microstructure. Figure 14 a/b shows FESEM-images of the microstructure of a glass component made by CerAM T3DP. The microstructure has a certain residual porosity. Optimization of the process parameters will help reducing the pores in future.

To evaluate the composition of the sintered glass microstructure EDX investigations had been carried out (Figures 15-18). Spectrum 1 (Fig. 16) shows an alumina impurity due to the powder manufacturing process. Spectra 2 and 3 (Figures 17 and 18) show the expected chemical composition.

## 4. Conclusions

Two Additive Manufacturing methods basing on photo-reactive suspensions (CerAM VPP) and on thermoplastic feedstocks (CerAM T3DP), respectively, which have been developed for ceramic manufacturing have been

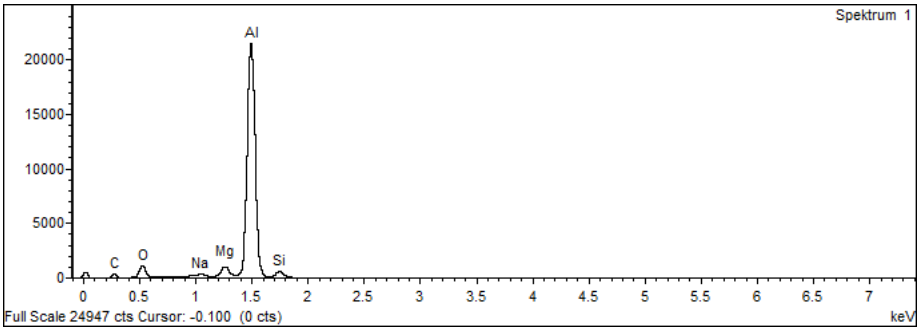



*Figure 16. EDX spectrum #1 of Fig. 15.*

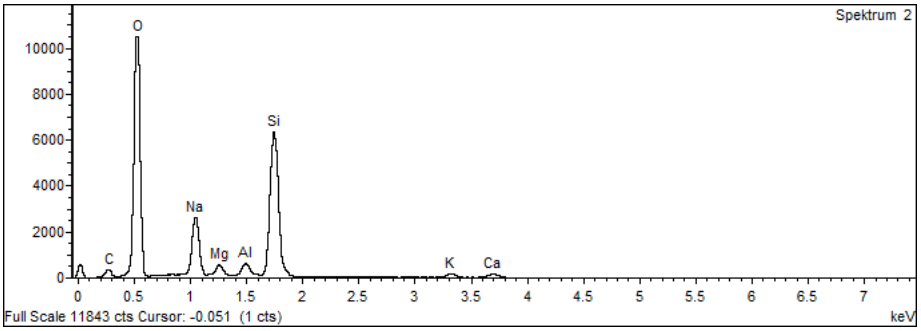



*Figure 17. EDX spectrum #2 of Fig. 15.*

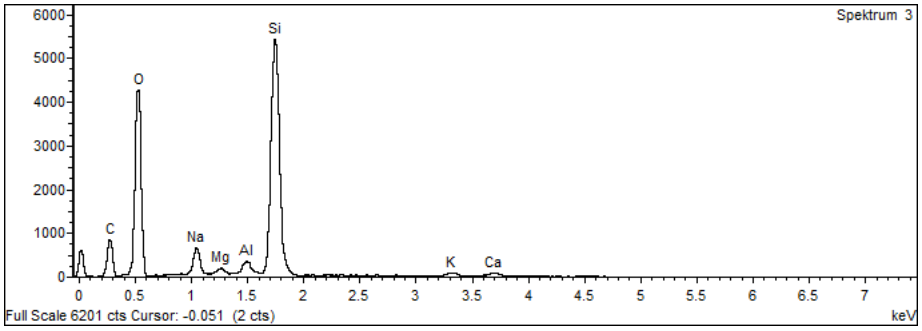



*Figure 18. EDX spectrum #3 of Fig. 15.*

applied to glass powder. Suitable light-curable suspensions and low viscous thermoplastic feedstocks were developed and used for manufacturing of different glass testing components. First experiments have been carried out with glass powders mixed with a certain content of luminescent pigment material. These functionalized mixtures could be successfully used for manufacturing of sintered glass components with luminescent properties by CerAM VPP. By means of both AM methods – CerAM VPP and CerAM T3DP, sintered glass components with densities higher than 99% of theoretical density could be attained which is comparable to injection molded glass components and even better than pressed sintered glass parts. Thus, ceramic AM technologies offer promising opportunities for manufacturing of functionalized glass components with extremely complex geometry.

**Acknowledgement**

Funding by the Fraunhofer Society within the frame of the Internal Programs is gratefully acknowledged.

**References**

[1] W. Vogel, Glaschemie, Springer-Verlag, 1992,3. Auflage.
[2] R.A. Eppler et al., Glazes and coatings, The Amercian Ceramic Society, Westerville, Ohio, ISBN 1-57498-054-8.
[3] E.M. Rabinovich, Review preparation of glass by sintering. J. Mater. Sci., 1985, 20, 4259-4429.
[4] H.E. Exner et al., A stereology based equation for isotropic shrinkage during sintering by viscous flow. In: Proceedings of Seventh World Round Table Conference on Sintering. Herceg-Novi, Yugoslavia. Plenum Press, New York, 1990.
[5] J. Frenkel, Viscous flow of crystalline bodies under the action of surface tension. J. Phys. Moscow, 1945, 9, 385-391.
[6] J.K. Mackenzie et al., Phenomenological theory of sintering. Proc. Phys. Soc. Lond., 1949, 62, 833-852.
[7] E.A. Olevsky, Theory of sintering: from discrete to continuum. Mater. Sci. Eng. R: Rep., 1998, 23, 41-100.
[8] T. Moritz et al., Glass Powder Injection Molding – Ceramic Processing Applied to Glass Components. Ceramic Applications, 2 (1), 44-49.
[9] T. Moritz et al., Material- and Process hybridization for Multifunctional Ceramic and Glass Components. Ceramic Applications, 2017, 5 (2), 66-71.
[10] J. Klein et al., Additive manufacturing of optically transparent glass. 3D Print. Addit. Manuf., 2015; 2 (3), 92-105.
[11] F. Kotz et al., Three-dimensional printing of transparent fused silica glass. Nature, 2017, 544 (), 337-340, doi:10.1038/nature22061.
[12] https://www.schott.com/tubing/german/products/properties/matched-sealing.html
[13] M.J. Pascual et al., Phys. Chem. Glasses, 2001, 42 (1), 61-68.
[14] Data sheet: LONG AFTERGLOW PHOSPHOR –TYPE HMK63D/L-L1, Norton Park, Norton Rd, Stevenage, Herts, SG1 2BB, England.
[15] U. Scheithauer et al.: Ceramic-Based 4D Components: Additive Manufacturing (AM) of Ceramic-Based Functionally Graded Materials (FGM) by Thermoplastic 3D Printing (T3DP), Materials, 2017, 10, 1368; doi:10.3390/ma10121368.
[16] U. Scheithauer et al., Investigation of Droplet Deposition for Suspensions Usable for Thermoplastic 3D Printing (T3DP). Journal of Materials Engineering and Performance, 2017, DOI: 10.1007/s11665-017-2875-4.
[17] S. Novak et al., The effect of water on the behaviour of alumina-paraffin suspensions for low-pressure injection moulding (LPIM). J Eur. Ceram. Soc., 2000, 20, 2175-2181.