# Additive Manufacturing of Functionalized Glass Components

**Additive Manufacturing (AM) processes for polymers, ceramics and metals have become increasingly important in recent years for the manufacture of near-net-shape components. In contrast, the use of glass for this technology has so far only been studied in isolated cases. Processing of glasses as powders by established ceramic shaping technologies and new AM technologies offer the potential for near-net-shaped complex components with additional properties. The integration of photoluminescent particles into the sintered glass matrices is used as an example to present the principle of functionalization and hybridisation of glass. Furthermore, the possibilities of co-sintering different adjusted suspensions and feedstock for the realisation of multi-component components will be demonstrated by the CerAM T3DP and der CerAM VPP technologies.**

In the conventional glass technology, besides the standard direct shaping of glass via the melt, there is also the possibility of shaping via the powder route. Tape casting is an established technology for the production of planar LTCC substrates from glass or glass-ceramic powders. Three-dimensional shaping using sinterable films is only possible to a limited extent, since complex components must be realised by combining laminating and structuring processes in conjunction with considerable mechanical effort (lasers, laminating presses, punching, etc).

Pressing of glass powders in the cold and hot state can also be regarded as established for the production of simple shaped components. For more complex components, complex post-processing must be carried out in the green or sintered state. Nevertheless, shaping of glass using the route of glass powders offers advantages over shaping from the melt. In particular, shaping at lower temperatures offers the option of manufacturing composite materials by using metallic or ceramic phases or carbon phases in combination with near-net-shaping technologies. By integrating inorganic additives into the feedstocks or slurries, properties of shaped parts such as thermal expansion behaviour, electrical conductivity or dielectric behaviour or optical properties can be modified. The AM of glass components is currently at a very early stage of development and is in most cases investigated from the glass melt, where the glass is deposited as molten strands or filaments [1].

A disadvantage of the process is the limited geometric freedom in the component design due to the extruded geometry and a corrugated surface structure of the components. The realisable complexity of components produced with this process can be estimated as comparable to conventional glass forming processes. On the basis of powder bed-based AM methods, glass powders have so far mainly been processed by Selective Laser Sintering (SLS) [2, 3, 4]. Mostly bioactive glass compositions were used, which were sintered by SLS to porous component structures. In [5], a borosilicate glass was processed into a porous filter component using this process.

To overcome the disadvantages of these shaping technologies for it is more convincible to adapt feedstock or slurry based technologies. Klotz, et al. demonstrated the use of nanoscaled fumed silica (dp around 40 nm) in combination with a UV-curable monomeric binder and a lithographic 3D-printing method to realise precise and complex shaped and fully densified transparent components made of pure silica glass [6]. However, this combination of binder and glass powder cannot be adapted to other commercial glasses or glass powders which are usually available as µm-scaled particles. Also the integration

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of other µm-scaled particles which enable the functionalization of sintered glass components such as electrical conductivity [7], luminescence or even coloration is not possible.

In making AM processes accessible to the wide range of glass powders with a wide spectrum of properties, processes are needed that enable the use of commercial standard glass powders. In order to meet the compromise between the sintering and softening temperatures well below 1000 °C on the one hand and a sufficient stability against environmental influences on the other hand, the glass 8250 from Schott/DE 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. 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. Fig. 1 shows a SEM-image of a glass powder received after milling of the coarse granules ($d_{10}$ = 0,8 µm, $d_{50}$ = 4,3 µm; $d_{90}$ = 10 µm,

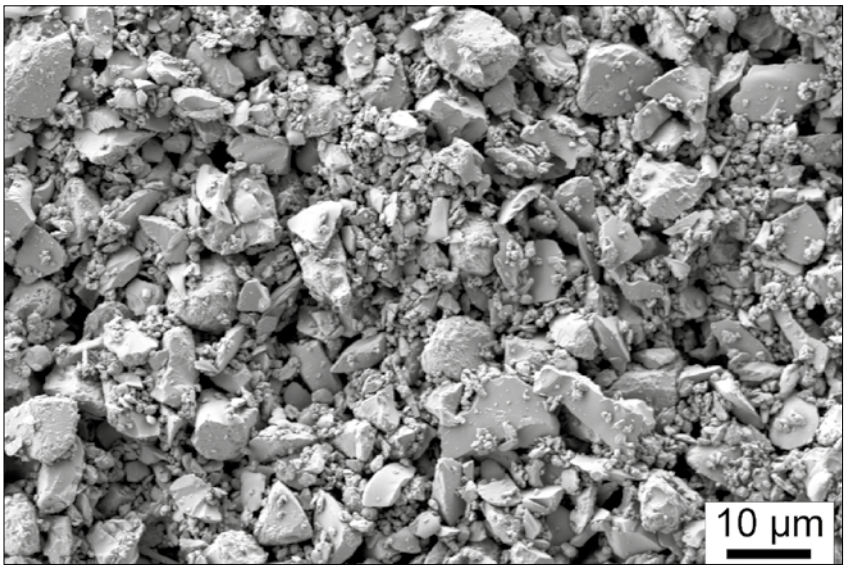


*Fig. 1*
*SEM-image of the 8250 glass powder*

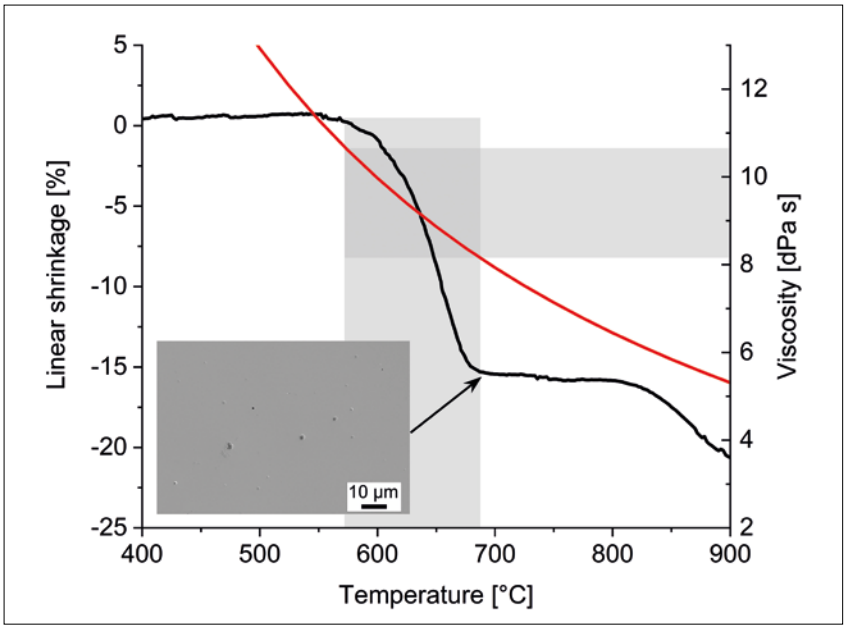


*Fig. 2*
*Sintering behaviour of 8250 measured by hot stage microscopy with corresponding plot of the viscosity data with a SEM image of the sintered microstructure of a powder compact*

$d_{99}$ = 14 µm). In contrast to typical ceramic powders, milling processes of glass frits end up with broadened particle size distributions and sparse shaped particles. Therefore, feedstock and slurry recipes developed for AM processes for ceramic powders like alumina have to be adopted and tuned for use in combination with µm-scaled glass powders in order to achieve processable viscosities and flow behaviour.

Within the scope of this work, the development of tailored slurries and feedstocks has been conducted for one suspension-based (Ceramic Vat Photo Polymerization – CerAM VPP) and one feedstock-based AM technology (Ceramic Thermoplastic 3D-Printing – CerAM T3DP).

**CerAM VPP**

CerAM VPP or also known as Lithography-based Ceramic Manufacturing (LCM) as the first commercialized AM method for making dense ceramic components bases on photo-polymerization of light-curable monomers under exposure to a certain wavelength. The light-curable binder system consists of a combination of different monomers.

In this publication, a CeraFab 7500 (Lithoz/AT) has been used. Using CerAM VPP requires an initial powder with a certain translucency for the wavelength which is applied for curing. CerAM VPP today offers the highest surface quality and the best resolution in ceramic AM. The production of dense (>99 %) glass components by using lithography-based AM technologies requires the development of special photoreactive suspensions curable at wavelengths of approx 452–465 nm. These suspensions should have a defined flow and curing behaviour, advantageously comparable to commercially available suspensions, to adjust the printing process parameters of the CerAM VPP process easily for them.

By tailoring the reactive binder system, new suspensions based on the glass 8250 were developed with the goal to maximise the sintered density and accuracy of printed components. In this study, suspensions with a solid content of approx 49 vol.-% were realised.

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 mass-% related to the photoreactive organic, camphorquinone as type II initiator was used. Additionally, a long chain polyethylenglycol was added as plasticizer.

**CerAM T3DP**

Thermoplastic 3D-Printing (CerAM T3DP) is a direct AM technology, which is developed at Fraunhofer IKTS/DE. The process is based on the selective deposition of single droplets of particle-filled thermoplastic feedstocks. This thermoplastic feedstocks contain different technical waxes, like paraffin or beeswax. Additives such as dispersants are used to stabilise the particles in the organic matrix. The solidification of the thermoplastic feedstocks is nearly unaffected by the physical properties of the used powders. So even metal, hard metal and glass suspensions can be fabricated and processed. By using up to four micro-dosing systems in one manufacturing device, it is possible to develop multimaterial components. CerAM T3DP uses micro-dispensing systems, which operate on the drop-on-demand principle and manufacture the components drop by drop.

Thus it is possible to deposit drops of different materials side by side. Typical solid contents of CerAM T3DP glass feedstocks are 36–55 vol.-%. The powder particle diameter may differ between a typical submicron powder and up to 5 µm. The nozzle orifice diameter is 100 µm, 160 µm, 200 µm or 300 µm optionally, and the deposition frequency applied for the thermoplastic ceramic suspensions is 80–120 Hz.

**Debinding and sintering**

After solidification, the near-net-shaped green parts are removed from the machine and undergo thermal debinding processes in furnaces similar to ceramic green components manufactured by this technologies. As already mentioned, due to softening behaviour of glasses which usually takes place several 100 K below the sintering of established Technical Ceramics special attention must be paid to the applied temperature regime. As a rule of thumb, the sintering of glass powders starts around 30 K above the glass transitions temperature $T_g$.Hence, the debinding step must be completed at a temperature around $T_g$ of the chosen glass and what in turn limits the number of glasses suitable for these AM technologies. In our case, the maximum allowed temperature for the debinding step lies at 480 °C.

After debinding, the so-called brown parts glass particle cohere by mechanical interlocking in a similar manner as ceramic

components do and the transfer of components to sintering furnaces is possible by careful handling without problems. In the last step, the debinded components are completely densified by a sintering process which can occur in a conventional muffle furnace as no special atmosphere is required and the maximum required temperature is below 700 °C. Typical heating rates range from 1–10 K/min depending of the size of the components and temperature distribution within the furnace. However, glass particles or powder compacts made of glass do not sinter as ceramics or metals do. The driving force for the sintering results from the viscous flow of the glass particles in contact with each other with the tendency to minimise the outer surface of the powder compact [8].

The sintering characteristics of a powder compact made of the glass 8250 is shown in Fig. 2 together with the corresponding viscosity data of this glass and an embedded SEM image of the microstructure of a sintered powder compact. The marked regions demonstrate, that within the effective sintering step about 2,5 decades of the glass viscosity from log $\eta$ = 10,6 to log $\eta$ = 8,2 are passed within a temperature range of 110 K. This in turn means that especially during the final step of the sintering process a precise control of the time-temperature profile is required. By exceeding the maximum sintering temperature or the dwell time, the viscous flow of the glass will lead to unwanted deformations of detailed features of the near net shaped components.

By applying optimised sintering profiles, it is possible to achieve fully densified microstructures of sintered glass powders within relatively short sintering times and without applying special atmospheres other than normal air at temperatures slightly below 700 °C. Due to the low sintering temperatures and short dwell time, it is possible to integrate particles with special properties into the microstructures in order to realise additional functionalities in the sintered components. This potential has already been successfully demonstrated in connection with the development of electrically conductive glass-carbon composites by powder injection moulding [9]. Within the scope of this study, the approach of integrating luminescent particles (phosphors) into a glass matrix in order to be able to combine the effect of afterglow with complex shaped components has been pursued. The advantage of integrating luminescent particles into custom-shaped components is that, for example, specific information such as icons, signs or words can be made visible even in dark environments. Such functions are important in safety-relevant areas, where people need to find their way in emergencies or receive certain information.

Where it is more important to manufacture this information or instructions in such a way that they have a high stability against environmental influences such as high temperatures, humidity and UV-radiation from the sunlight. One the one hand, integration of such luminescing particles in organic matrices such as polymers is in principle also possible, but the property profile of such components

are limited by the stability of the polymer. On the other hand, a co-sintering process with Technical Ceramics such as alumina is not possible as the materials lose their luminescent properties at high temperatures. So it is convenient to think about an inorganic material which can be used as a stable matrix for these luminescent particles and can be processed at temperatures well below 1000 °C. In view of the aforementioned boundary conditions, the 8250 glass offers a material for a matrix that can be sintered within these temperature limits and has a better stability than most polymers.

Within a set of principle experiments, the effect of diluting photoluminescent particles in a glass powder and the sintering step at 700 °C on the afterglow behaviour has been investigated. Commercial alkaline earth aluminate long after glow phosphor powders BGL-300FF and GLL-300FF were used. The material GLL-300FF has a yellow-green emission colour with an emission peak at 521 nm and BGL-300FF a blue emission colour with an emission peak at 491 nm [10, 11]. The particle diameters of both photoluminescent powder qualities range between 3,3 µm for the $d_{50}$-value and up to 13 µm for the $d_{100}$-value. Powder mixtures of the phosphor powder GLL-300FF and the 8250 glass powder were prepared in graduated proportions of phosphor between 5–50 mass-%. The afterglow behaviour of the powder compacts of the mixtures has been analysed by UV/VIS spectrometry in the reflection mode after sintering at 700 °C.

For the purpose of illustration, Fig. 3 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. From the plotted data it can be seen that even a content of 5 mass-% of the phosphor is sufficient to achieve a detectable afterglow effect. The comparison of the luminescent behaviour at the detection wavelength of 520 nm of the powder compacts before and after sintering in Fig. 4 demonstrates that a thermal treatment at 700 °C does not affect the visible after glow behaviour. Measurements of the density of sintered powder compacts reveal a densification up to 97 mass-% of the theoretical density by adding a content of 30 mass-% of the photoluminescent particles without any modifications of the sintering profile.

## Development of suspensions and feedstocks

Based on these results, the development of suspensions for the CerAM VPP process and feedstocks for the CerAM T3DP process was started. The development of the CerAM VPP suspension started with the selection of a light-curable binder system, which is composed of a crosslinking system comprising at least two multifunctional acrylates to build up the polymer matrix, a monofunctional 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 for easier debinding. The organic components and the described glass powder were mixed to create a suspension by processing them with a high speed planetary ball mill (Thinky ARV 310, C3-Prozesstechnik/DE). The homogenization and a degassing step (30 mbar) of the mixture were carried out in four steps: (i) 4 min at 1000 rpm, (ii) 45 s at 1500 rpm, (iii) 30 s at 2000 rpm and (iv) 15 min at 200 rpm for degassing. After preparation, the suspensions were characterised in terms of their rheological properties as well as the curing behaviour in order to determine optimal CerAM VPP parameters like curing time and process duration. For illustration purposes, Fig. 5 compares the structure of a green body and a sintered glass sample made by the CerAM VPP process. The sparse glass particles with their wide particle size distribution are sintered through the viscous flow forming a dense microstructure exhibiting only a few residual spherical pores.

AM of complex glass components with luminescent properties by using the CerAM VPP technology requires the modification of the recipe for the single component glass suspension. For this purpose, a part of the glass powder within the suspension must be replaced by the above describe luminescent particles.

Two different suspensions with a concurrent sintering behaviour were developed,

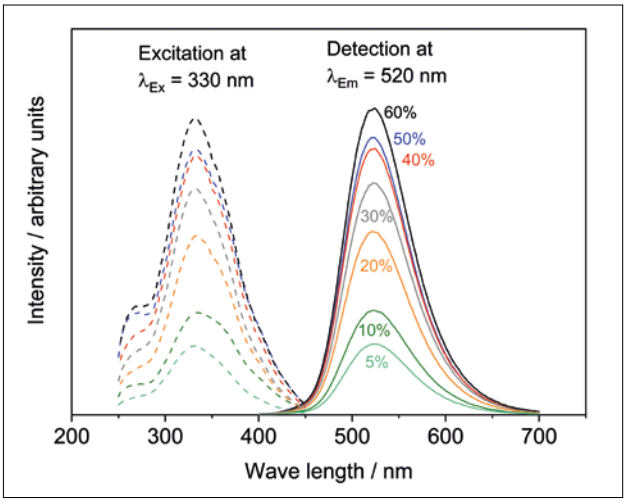


*Fig. 3*
*UV/VIS spectra of the excitation and emission behaviour of powder mixtures made of the luminescent powder GLL-300FF and 8250 glass powder*

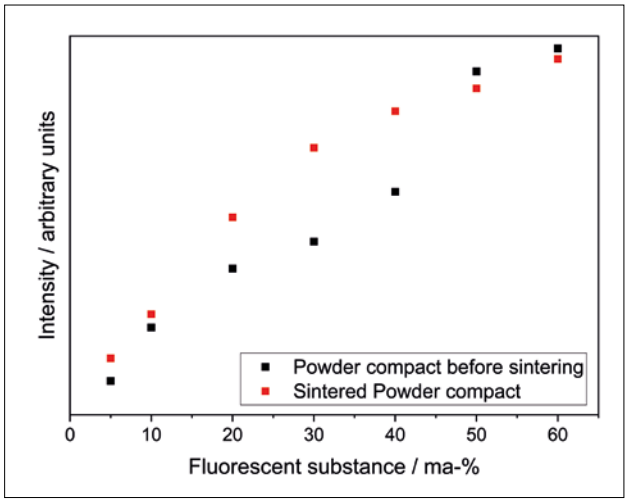


*Fig. 4*
*Comparison of the photoluminescent GLL-300FF after glow behaviour at 520 nm of powder compacts, before and after sintering*

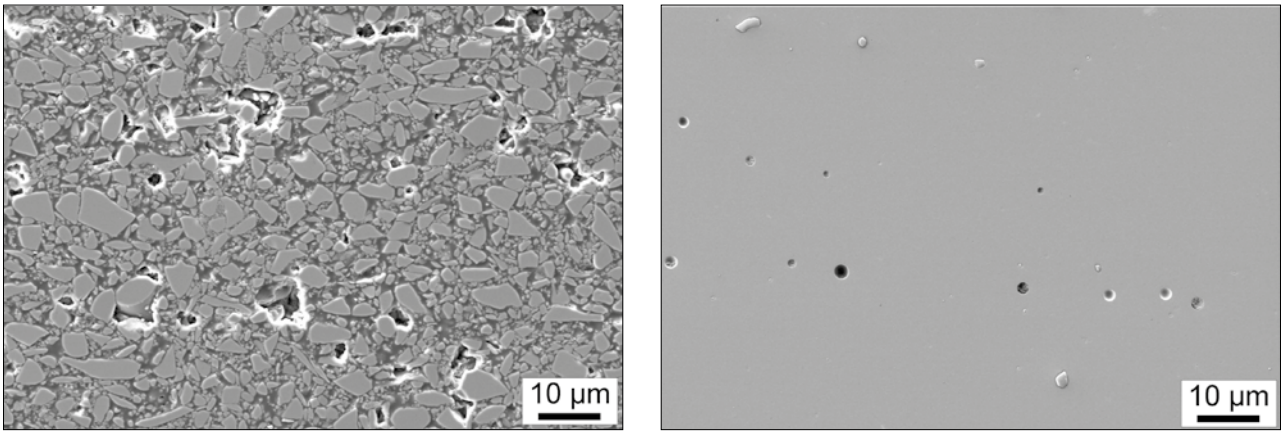


*Fig. 5 a–b*
*Green (a) and sintered (b) microstructure of the 8250 glass powder shaped by the CerAM VPP-process*

one based only on glass and the second by replacing 20 mass-% of the powder material by the photoluminescent powder. This amount of photoluminescent particles was selected on the basis of the sintering results of the binder-free powder mixtures described above and is intended to ensure that dense sintered components are obtained. Due to the similar particle sizes of the photoluminescent particles, both suspensions show similar shrinkage during the sintering process. In this way, the realisation of co-sintered composite components from suspensions with different functions or properties is enabled. In our case, this option can be used to produce, for example, luminescent signs or icons with a signal effect entirely from durable glass.

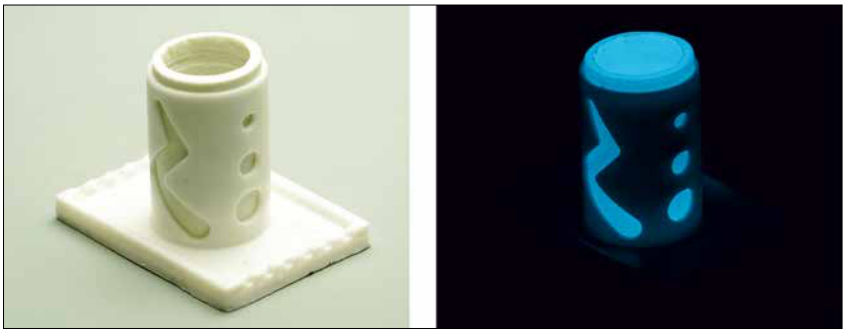

*Fig. 6*
*CerAM VPP component made of 8250 and photoluminescent particles*

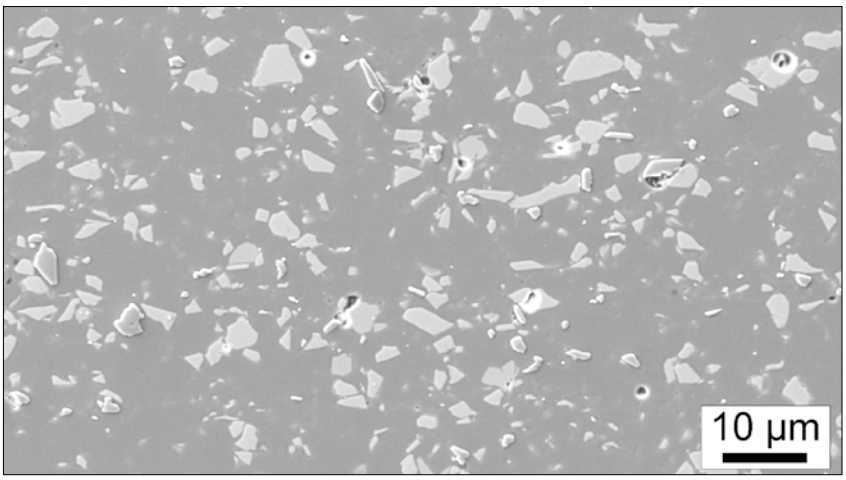


*Fig. 7*
*SEM-image of a sintered CerAM T3DP-component containing photoluminescent particles*

After preparation, both suspensions have been characterised regarding their flow behaviour and curing characteristics on one hand to quantify the influence of the luminescent particles and on the other hand to estimate the printing parameters, which means vat rotation speed and curing time. In general, the dynamic viscosity of the luminescent glass suspensions was comparable to the pure glass suspension and an adjustment of the vat rotation speed was not necessary. Due to the luminescent filler particles the absorption for visible light was increased resulting in a different curing behaviour compared to the pure glass suspension. For reaching a comparable layer strength, the exposure intensity and time had to be increased. Based on the characterisation results, the printing parameters were adjusted and test components with luminescent properties (Fig. 6) were printed with high contour accuracy.

Debinding and sintering were done in conformity with the pure glass components. The photoluminescent after glow effect is well seen in the right image taken in a complete dark environment. For illustration, Fig. 7 shows the microstructure of a glass matrix composite containing 20 mass-% of the photoluminescent particles after sintering at 700 °C.

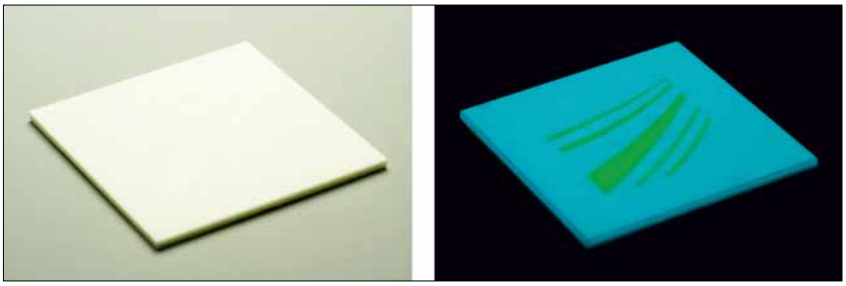

*Fig. 8*
*T3DP-component made of 8250 and 2 types of photoluminescent particles (blue and green)*

In case of the T3DP method for the preparation of dispensable glass suspensions, the binder system had to be completely redeveloped. The binding system consists of various technical waxes and other stabilizing additives. The waxes with different decomposition temperatures are necessary to debind the manufactured components without defects.

Due to the relatively low sintering temperatures, it had to be ensured when selecting the binder components that no organic residues are present at a temperature of 450–500 °C. In addition, the composition of the thermoplastic feedstock must be chosen so that when changing the physical states no stresses occur in the component.

Mixing and homogenization of the thermoplastic suspensions takes place in high-speed mixers like Dispermat CA-20C (VMA Getzmann GmbH/DE) or, for larger batches, in heated ball mills. The proportion of organic additives of thermoplastic glass suspensions is between 45–64 vol.-%. Thus, the viscosity of the feedstock is relatively low, showing a shear-thinning flow behaviour and processable already at approx 100 °C.

By using the CerAM T3DP, multimaterial glass components can be produced directly in one production step. For such a multicomponent manufacturing process, it is necessary that the used thermoplastic feedstocks show an almost identical shear thinning flow behaviour.

This is reflected in the droplet formation during the printing process. In order to produce dosable luminescent feedstocks, the composition specially developed for glass must be adapted accordingly. For this the content of solids must be reduced. Instead of the glass powder the GLL-300FF (green) or the BGL-300FF (blue) photoluminescent particles are added as appropriate. For the realisation of even layer heights, both feedstocks must have almost the same droplet characteristics. By means of a detailed parameter study, corresponding process parameters have been determined.

In order to realise a multimaterial luminescent component using CerAM T3DP, separate CAD files must be available for each component. This can be done in the form of single STL-files or with an appropriately configured 3mf-file. In a corresponding slicing software, these files are assigned to a specific print head and the associated material suspensions. With the developed thermoplastic feedstocks and the determined process parameters different structures can be produced additively (Fig. 8). The green bodies existing after the manufacturing process are then debinded and sintered like the pure glass components.

The processing of glass via the powder route as a single phase component or as a matrix phase in functional multimaterial components has only been established to date with shaping processes that allow components with relatively simple geometries.

The realisation of complex near-net-shape components is achieved by using AM processes, as this study exemplarily demonstrated by means of Schott glass 8250 and photoluminescent particles. A transfer to other glasses should be possible as long as the sintering temperatures are above the debinding temperature and no undesired crystallization occurs during sintering.

In contrast to many ceramic materials, however, only a narrow temperature window is available for sintering of glass powders, which is defined by their viscosity characteristics. With the variety of available glasses and their applications, a new class of materials is available to AM processes, which also enables hybridization by integrating functional particles in starting powder mixtures.

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