Preparation of glasses by sintering of nanosized particles

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The sintering of nanoscaled glass powders offers new possibilities for the preparation of bulk glasses and glass coatings because the maximum processing temperature can be significantly reduced compared to the traditional melting technique. Nanoscaled glass particles are necessary if a compact should be completely densified to a transparent glass body by sintering below the crystallisation temperature. According to the optical fibre technology where high-purity silica glasses are prepared starting from gas-phase deposited, nanoscaled silica glass particles, the forming methods known from ceramic technology were adapted to pure and doped fumed silica powders. Thus complex shapes of glass bodies and could be prepared without moulds.

For the preparation of thick glass coatings (10 - 500 µm) on a substrate glass the decrease of the processing temperature is of great importance. Due to reduction of the processing temperature of nanoscaled glass, glass components, which lower the viscosity (like lead oxide) can be omitted and, consequently, the chemical resistance is not reduced. For these thick glass coatings the thermal expansion coefficient has to be matched to the substrate glass. As these multicomponent glass powders are commercially not available, it was shown that these powders can be synthesised by a modified flame hydrolysis. For a borosilicate glass powder the processing temperature for complete densification could be decreased to approx. 700 °C.

Introduction

Glasses are generally prepared by melting raw materials or glass powders. An alternative process for advanced materials is sintering of compacts made from nanosized powders. This sintering route was pushed forward for the preparation of high-purity glasses for optical fibres, where nanosized silica glass powders were used due to the short diffusion path of the impurities inside these small particles.1 Compacts were prepared by direct gas phase deposition or, alternatively, by colloidal processing 23456of fumed silica, and sol-gel processing78. It was shown that the properties of sintered silica glasses could be widely changed leading to further applications9.

Besides bulk glasses the preparation of thick glass coatings (10-500 µm) via sintering of nanosized glass powders is also of interest]10. Glass powders for enamels and glazes are generally prepared by grinding. Therefore the particle size is typically larger than 10 µm and, consequently, these powders have to be densified by melting, which needs viscosities of the coating glass of less than 10^4 dPa·s. As for technical glasses the maximum processing temperature is limited to 500 - 700 °C, the viscosity of the coating glass has to be reduced significantly compared to the substrate glass. Otherwise problems with the distortion of the shaped glass body may occur. The lowering of the viscosity is achieved with a „chemical compromise“ because with these network modifiers, which lower the viscosity, the chemical durability of the glass is also decreased. For nanosized, sintered glass particles the processing temperature can be reduced without this „chemical compromise“. For thick coatings on substrates of technical glasses the thermal expansion coefficient of both glasses has to be adjusted. Therefore fumed silica powders are no longer applicable and multicomponent glass powders have to be used. Unfortunately, nanoscaled multicomponent glass powders are not yet commercially available.

It is the objective of this paper to review this sintering route showing the specific problems during processing as well as the perspectives for new applications of nanosized powders.

Fundamentals of processing nanopowders

In contrast to the conventional melting of glass which needs high temperatures during refining to reduce the viscosity of the glass melt to 10-100 dPa·s, the maximum processing temperature during sintering of nanosized glass powders is significantly reduced. With these particles sintering takes place at viscosities of $10^9...10^{12}$ dPa·s. The difference between melting and sintering is schematically shown in fig. 1 according to the viscosities of 4 technical glasses. Although all glass powders densify via viscous flow at elevated temperatures the term "sintering" is used in this paper only for this viscosity range.

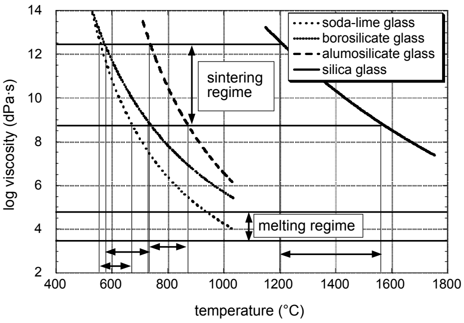


Fig. 1 Definition of melting and sintering regime of glasses according to viscosity

For a complete sintering of a compact to transparent glass via viscous flow, nanoscaled glass particles are necessary because otherwise the critical crystallisation temperature is exceeded. Heat treatment during sintering of glass powders differs from the melting of glass. During sintering the temperature of the compact is raised after shaping at room temperature, while for the conventional hot-working of glass the temperature is lowered from the molten glass. Consequently, the critical areas of crystal growth and seed formation are passed in opposite directions. The sintering regime is limited by crystallisation temperature. This is schematically shown in figure 2. The complete densification of a compact to transparent glass can be only achieved if the sintering temperature is lower than the crystallisation temperature. For that the particle size of the glass powders has to be very small. If the seed formation is very low which might be achieved in high-purity glasses (like silica glass) or with high heating rates in the seed formation area, the maximum processing temperature can be increased. Therefore the temperature treatment and the particle size of the compact are dominating factors for the sintering behaviour and the possibility to get a transparent glass by sintering. It should be kept in mind that for conventional heating in a furnace the temperature inside the sample depends on the thermal conductivity, which is rather low in compacts made from nanosized powders11.

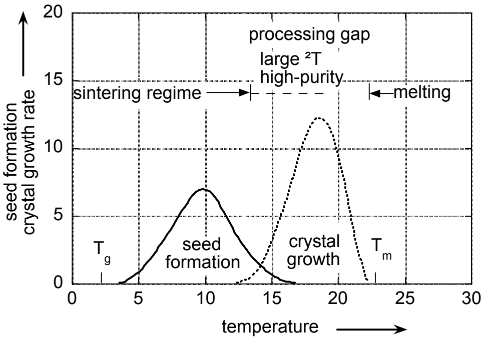


Fig. 2 Different heat program for sintering and melting of glasses

Processing of nanosized powders

The production of optical fibres is one of the most important examples for the preparation of advanced materials starting from nanosized particles. As these activities started on research level already 1970, these processes are much older than the term "nanotechnology". A brief presentation of four important production processes is given in fig. 3. While in inside processes like PCVD and MCVD the generated particles are directly consolidated on the substrate glass, in OVD and VAD compacts of nanosized silica particles are formed, which are finally sintered to transparent silica glass. Due to the small diffusion path in nanosized glass particles in a compact with open pores, impurities can easily removed in a reactive atmosphere like chlorine before sintering leading to a high-purity glass (impurity level < ppb). This big advantage led to the break-through of this new method.

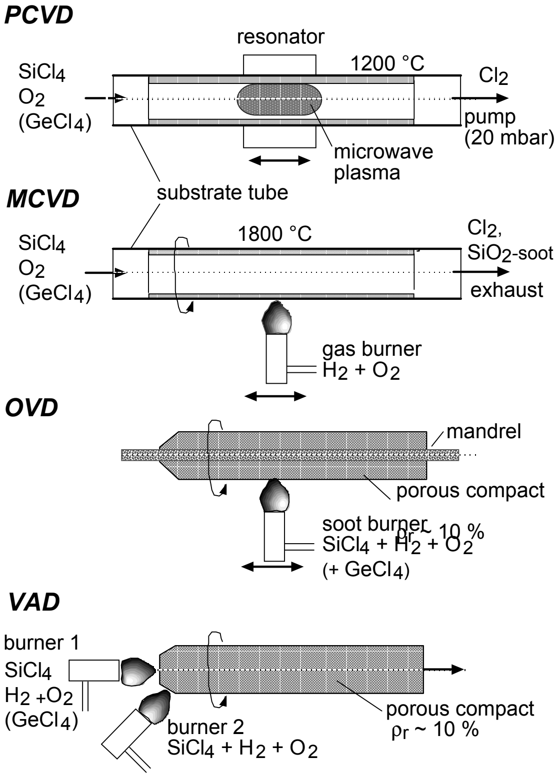


Fig. 3 Schematic presentation of the most important processes for producing optical fibres for telecommunication

The separation of powder synthesis and shaping of compacts into two processing steps offers a higher flexibility for the preparation of compacts with more complex shapes or new properties for further applications. The processing scheme is shown in fig. 4. For the preparation of sintered glasses a high green density is advantageous to reduce shrinkage and to reach near net-shape. In contrast to this for aerogels a very low green density should be reached. If modification of the compact with a gas-phase reaction is planned, a medium green density should be favoured because the gas exchange in the small pores correlated to high green densities is very low (Knudsen regime). A third process direction is shown in the upper right, where functional nanoparticles are incorporated into the glass matrix. In case of making high-density compacts nanosized particles are only used to reduce processing temperature. After sintering a homogeneous glass is formed and, in contrast to ceramics, no grain size correlated to starting powders can be detected anymore.

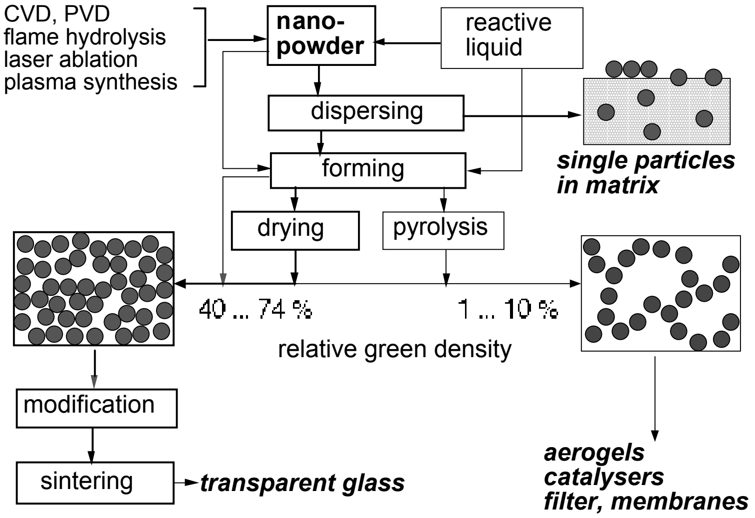


Fig. 4 Processing scheme for sintering glasses from nanopowders

For preparation of glasses via this sintering route a convenient nanosized starting powder is needed. There are a lot of synthesis routes, which been tested for preparing nanosized powders:

- vacuum deposition (evaporation, sputtering, noble gas condensation)
- gas phase deposition (flame hydrolysis, laser ablation, plasma burner)
- chemical reaction (sol-gel method, emulsions method, pyrolysis)
- electrochemical methods
- mechanical methods (ball mills)

It is important that the starting powders are non-porous, glassy, and should contain no organic contaminations. This is a general problem in wet chemical synthesis methods. Fumed silica powder is a well-suited and inexpensive starting material, which is produced in a variety of specifications via flame hydrolysis on an industrial scale. From these commercially available powders Degussa Aerosil OX50 is most convenient due to its relatively large particles size of 10 to 100 nm. Compared to finer powders like Aerosil A200 the problems with shrinkage during drying are much smaller with Aerosil OX50..

Compacts of Aerosil OX50 can be prepared by different methods. Convenient methods should start from suspensions with low viscosity because in this case it is easier to separate aggregated particles. this is very important to achieve a homogenous compact after shaping. Some examples are:

- particulate gelling (starting from nanosized particles)
- sol-gel method (starting from solutions)
- electrophoretic deposition from suspensions

Forming of particulate gels (coagulation process) is a very simple method, where 0.75 wt.-% NH_4F is added to an aqueous suspension of 50 wt.-% Aerosil OX5012. Due to the high thixotropy of this suspension it shows a low viscosity under shear stress (typ. 10 -50 mPa·s) and can be poured into a mould. Under resting the suspension coagulates and the stiffened body can be removed from the mould (schematically shown in fig. 5). Hereby any shear stress has to be avoided. Therefore the improvement of the mechanical strength would be desirable. This can be achieved by adding a binder, which polymerises after the suspension had been poured into a mould (like the Lucent process according to U.S. patent 5 240 488). For that 46 g Degussa Aerosil OX50 (46 m^2/g) were dispersed in 54 mL pure water 5 mL tetramethylammonium hydroxide (TMAH; 25 % in water). Then the binder was added which consisted of 0.1 g polyethyloxazoline, 0.4 g glycerine, and 0.96 mL methyl formate. This suspension was poured into a mould directly after mixing the components. After some minutes the suspension gelled and the stiffened compact could be removed from the mould after 10 min. The compact was dried at ambient atmospheres and heated for 4 h at 500 °C in air to remove the binder. The relative green density was 36.8 %, which is approximately the same like the compacts made by the coagulation method with NH_4F.

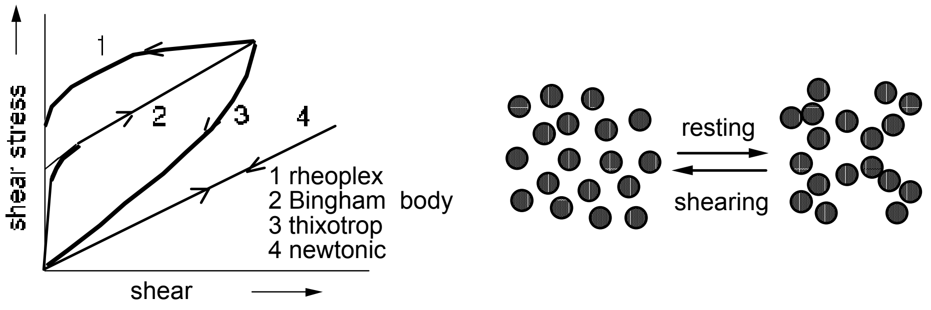


Fig. 5...Mechanism of forming particulate gels via coagulation

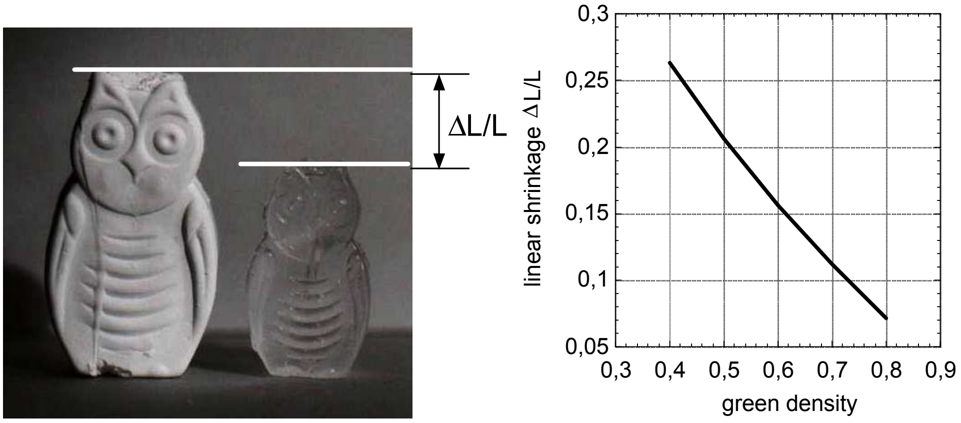


Fig. 6 Shrinkage ΔL/L during sintering (left) and correlation of green density and shrinkage (right)

In fig. 6 a compact with complex shape prepared by this binder method is shown on the left side. This shaped body was isothermally sintered at 1500 °C (10 K/min) in air. Even with this simple method transparent silica glass was obtained. At the right side of the picture in fig. 6 the owl is shown after sintering. Sintering in helium or vacuum improves the glass quality. The high shrinkage during sintering can clearly be seen. This shrinkage is directly correlated to the green density of the compact. This is shown in the diagram in fig. 6 based on a simple calculation.

A significant increase of the green density can only be achieved if coarser particles are added to the nanosized powders like Aerosil OX50. It is well known that bimodal or trimodal particle size distributions can increase the green density even above the hexagonal dense packing of spheres (74 %). Thus silica compacts with densities of 80 % (and more) could be achieved resulting in a drastically reduced shrinkage during sintering. An example is shown in fig. 7. The added coarser particles increase the sintering temperature necessary for transparent glass. As a higher green density reduces sintering temperature on the other hand, in total there is only a slight increase of sintering temperature for these high-density compacts of approx. 50 °C.

Fig. 7 Parrots with reduced shrinkage. Green body (left) and sintered glass (right)

Modifying compacts

One big advantage of the sintering route for preparing glasses is a large variety of possiblities for modifying the properties. Beside the well-established purification in a reactive atmosphere, which is state of the art for optical fibres, all kinds of dopings can be applied via the open pore structure of the compacts. This is schematically shown in fig. 8. While for well-known ruby glasses or red CdS/Se glasses the colouring component has to be solved in the molten glass, for sintered glasses the second component has only be incorporated via a solution or suspension into the open pores. After drying of the solvent the pore size of the compact determines the size of the functional nanosized secondary phase if no percolation occurs during drying. It is much easier to control the pore size of a compact compared to the seeding and crystal growth process in the melting route. Furthermore, gradients or local structures can be easily

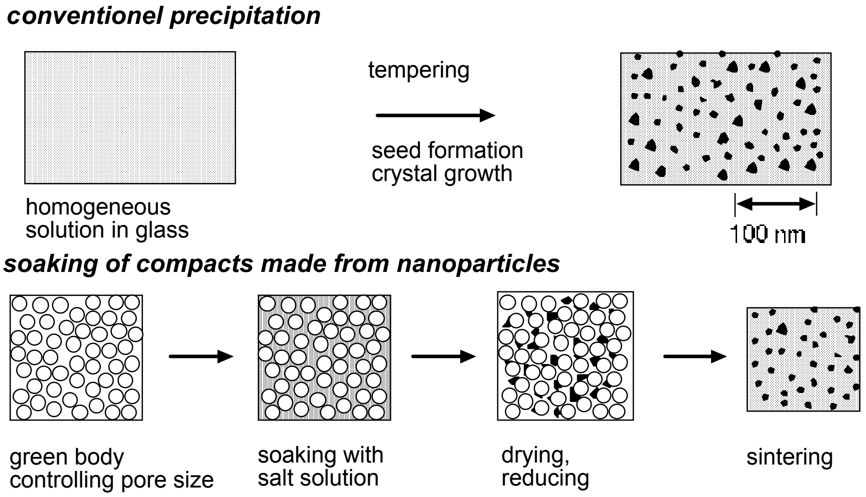


Fig. 8 Schematic comparison of conventional and pore sized controlled preparation of nanosized secondary phases inside a glass

achieved. Due to this high number of possibilities to modify a compact only a brief summarise can be given:

- preparation of nanocomposites
- gradient materials
- glass-metal composites (e.g. combining electrophoretic deposition and electrodeposition

Preparation of coatings of nanosized powders

Besides the preparation of near net-shaped glasses via the described sintering route thick coatings (typically 10 -500 µm) are of great interest. In many cases it is much easier to modify the properties of a material by coating instead of changing the complete bulk volume, especially if rather expensive nanosized powders are used. For coatings of fine powders on a substrate, the maximum sintering temperature might be additionally limited by the substrate. A summary for different substrate materials is given in fig. 9. There are no severe problems for glazes on ceramics and enamels on steel, but for technical glass substrates there are restrictions. In this case the reduction of process temperature due to nanosized particles is of great importance instead of using glass component which reduce viscosity and, consequently, chemical stability. This point was already mentioned in the introduction.

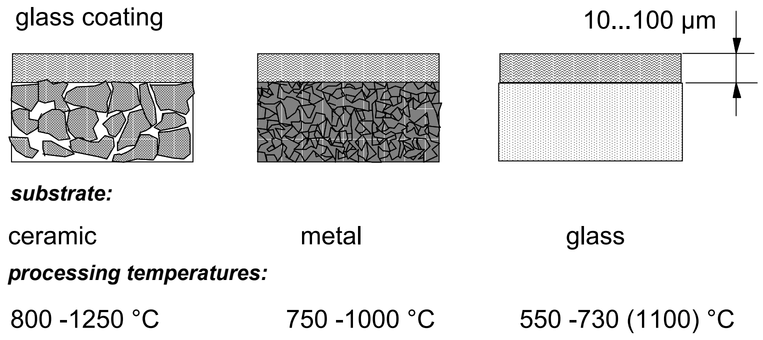
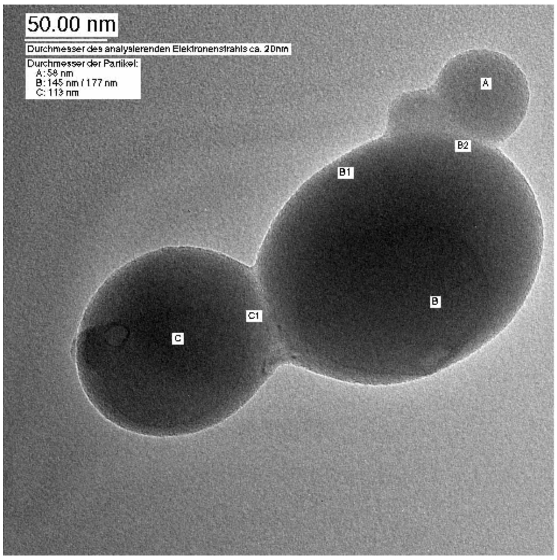


Fig. 9 Condition for glass coatings on different substrates



EDX-analysis (calculated for oxides) [wt.-%]	A	B	B1	B2	C	C1
SiO_2	81,5	92,4	85,6	84,4	76,6	71,1
Na_2O	1,0	0,3	0,7	1,0	1,0	1,8
B_2O_3	17,5	7,1	13,7	14,6	22,4	27,1

Fig. 10 HRTEM multicomponent glass powder (top) and table with analysis (bottom)

For thick glass coatings the thermal expansion coefficient of the coating glass and substrate glass has to be adjusted. Therefore fumed silica powders are no longer applicable and methods had to be developed for the preparation of multicomponent nanosized glass powders. This field is still under investigation and only first results can be reported here. By a modification of the flame hydrolysis process it could be demonstrated that nanosized particles with all typical glass components like SiO_2, Na_2O, CaO, Al_2O_3, B_2O_3 can be generated and deposited directly on a substrate. In fig. 10 the chemical homogeneity of a three component glass is shown.

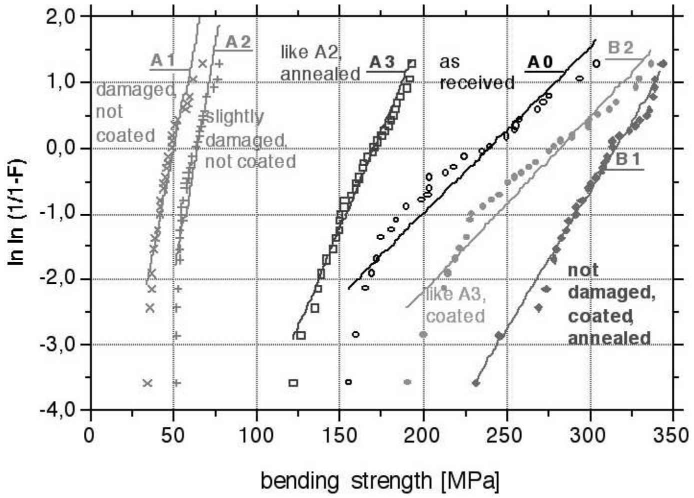


Fig. 11 Weibull plot of sintered borosilicate nanoparticle coating on soda lime glass[13]

A first application of such coatings for improving mechanical strength of a standard soda lime glass is shown in fig. 11. The coating was prepared by depositing a white soot layer on a cold substrate, which was isothermally sintered at 720 °C to a transparent glass layer. The borosilicate glass coating (composition approx. 80 % SiO_2, 15 % B_2O_3, 2 % Na_2O, 3 % Al_2O_3) improved the mechanical strength.

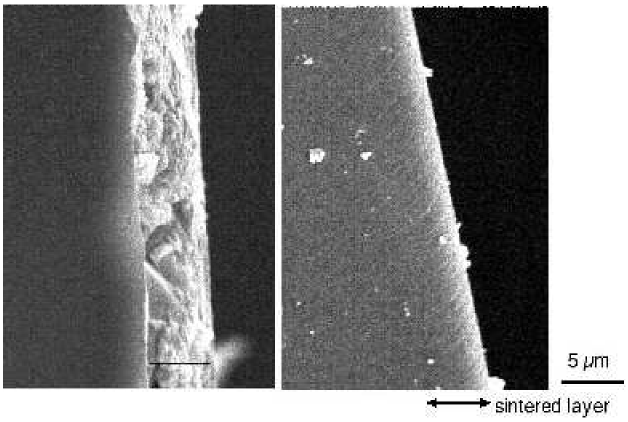


Fig. 12 Nanopowder coating on glass substrate before (left) and after laser densification (right)

Another example is shown in fig. 12. Here emphasis was laid on the crack-free coating of a borosilicate glass substrate with nanosized glass particles. After drying this coating was densified to a dense glass layer in a temperature gradient with a CO_2-laser.

Conclusions

The preparation of glasses via the sintering route of nanosized particles offers new perspectives because the processing temperature can be significantly reduced compared to the traditional melting. For silica glass a reduction from 2200 to 1200-1550 °C is observed. Due to the shaping at ambient temperatures near-net form shaping is possible in contrast to the hot working of molten glass. This was shown for silica glass, which was completely sintered from a compact with complex shape made from fumed silica powder (Aerosil OX50). Adding of coarser silica glass particles reduced the shrinkage of the compact during sintering down to 4 % (linear) with only a slight increase of sintering temperature. The open pore structure of these compacts can be used for doping or preparing composite or gradient materials.

For thick glass coatings (10 - 500 μm) on glass substrates the reduced processing temperature is also of great interest because glass components like PbO which decrease viscosity can be avoided. For coatings on technical glasses the thermal expansion coefficient of the coating glass has be adjusted. Therefore multicomponent nanosized glass powders are necessary. The feasibility of preparing nanosized particles by modified flame hydrolysis and efficient laser sintering was finally shown.

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