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Manufacturing of pure and doped silica and multicomponent glasses from SiO_2 nanoparticles by reactive electrophoretic deposition

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Abstract Manufacturing of glasses by shaping of powders and sintering comprises several advantages, like near-shaping of complex structures. Furthermore, sintering to fully transparent glasses is typically obtained at temperatures significantly lower than via melt fabrication. Thus incorporation of functional dopants with lower decomposition stability becomes possible, significantly increasing the variety of possible doping materials and applications. However, nanosized particles with their significantly enhanced sintering activity have to be used for powder manufacturing of glasses to avoid crystallisation. Unfortunately, no suitable nanopowders with appropriate composition are commercially available, and the manufacturing techniques proposed so far are complicated and time-consuming, often resulting in inhomogeneous doping. In contrast, by means of the newly developed reactive electrophoretic deposition (EPD) fast shaping and doping of glasses in only one process step is possible, using pure nanosized fumed silica powders as starting material. Doping is achieved by electrophoretic co-deposition of the nanoparticles and functional ions, surrounding each particle homogeneously in the electrochemical double layer. Thus doping with anions as well with cations was possible, resulting in different colouration of the silica glass (blue or gold ruby), with the coefficient of absorption being a function of the ion concentration within the suspension. Furthermore, a decrease in sintering temperature was achieved by EPR with boric acid. Finally, co-doping with anions and cations resulted in the manufacturing of multicomponent glasses with a decrease in sintering temperature of 450 °C compared to pure silica OX50.

Introduction

Compared to conventional melting technology, manufacturing of glasses from nanoparticles offers several advantages. First of all, a better shaping is possible because suspensions have a lower surface tension (app. 70 mN/m for an aqueous suspension) than molten glass (340 mN/m for a silica melt) [1]. As a result, complexly shaped glasses with sharp edges can be fabricated without cost-intensive post-processing [2]. Secondly, sintering temperature is much lower than melting temperature for a given glass composition. Maximum temperatures in melt fabrication of silica glasses are app. 2,200 °C and shaping has to be carried out at temperatures between 1,700 °C and 2,100 °C. In contrast, a green body shaped at room temperature from fumed silica (Degussa Aerosil® A380) with a mean particle size of 7 nm is sintered to full density at a temperature of 1,250 °C [3]. Since shaping can be carried out at room temperature using powder processing, inexpensive polymers can be used as mould materials, reducing the production cost significantly. In contrast, tungsten alloys or graphite are typical mould materials used in melting route, which bear the danger of contamination of the glass and with the further disadvantage of high wear due to the highly corrosive

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silica melt. While in melt fabrication of glasses crystallisation is not a severe problem because the temperature regime of seed formation is reached at lower temperatures than the range of crystal growth, a more sophisticated process control has to be applied during sintering to avoid crystallisation. Here temperature is increased during sintering and consequently the temperature range of seed formation is reached first and with further increasing temperature these seeds can grow. To avoid crystallisation sintering temperature has to be lower than the range of crystal growth. This can only be achieved if very fine or nanosized particles are used because the sintering activity increases above average with decreasing particle size due to the significantly higher specific surface area. As mentioned above a fully dense and transparent silica glass is achieved after sintering of an A380 (7 nm) green body at 1,250 °C [3], after sintering of an OX50 (Degussa, 40 nm) green body at 1,320–1,450 °C (depending on shaping technique) [4] and after sintering at 1,620 °C (in vacuum to avoid crystallization) of a green body shaped with 15 μm sized SE15 (Tokuyama) [5]. Although as low a sintering as possible is important regarding pure silica glass with its very low crystallisation rate, it is even more crucial for doped silica glasses or multicomponent glasses where crystalline secondary phases within the green body (e.g., dopants) can promote crystallisation by secondary seed formation.

Furthermore, sintering at significantly lower temperatures compared to melting route offers one more important advantage. The variety of dopants is much less limited because compounds with lower temperature stability can be used, which otherwise would evaporate in melt fabrication.

In case of sintering technology, functional nanosized secondary phases can be incorporated into the glass network by impregnation of the open porous green body prior to or during sintering. Impregnation can be achieved from the gas phase by different CVD techniques, by soaking with salt solutions or by incorporating nanosized solid particles. However, the pore size of green bodies consisting of nanoparticles is typically in the same range as the mean free path of the gas molecule (Knudsen flow), resulting in very slow impregnation of large bulk materials [6]. By soaking of green bodies with salt solutions much more different doping materials can be incorporated, first as ions into the green body and subsequently into the glass network during sintering. Thus gold ruby silica glasses were prepared by soaking a silica green body with a gold chloride solution. After drying at room temperature the green body was sintered at 1,250 °C. In this last step of the process, gold colloids having a size of 10–30 nm were formed while the glass is completely densified [7]. However, a homogeneous doping can only be achieved for very small components. Otherwise a gradient of the dopant concentration has to be accepted as a result of the osmotic transport of the ions from bulk towards surface during drying. This behaviour is demonstrated in [8] where a silica green disc (100 mm diameter) is soaked with a cobalt chloride solution and dried at ambient temperature resulting in a higher concentration of cobalt at the edges and a depletion in the middle of the disc and thus an inhomogeneous blue coloration after sintering. One possible solution is the use of reactive or sol-gel solutions for soaking, where a reaction of the solution at the internal interfaces of the green body (pore channel walls) or a reaction of the sol with water inside the pores result in an immobilization of the dopant phase inside the green body [8]. However, a homogeneous reaction front has to be achieved throughout the whole cross section of the green body to allow a homogeneous doping, which is very difficult to achieve. Furthermore, this method comprises two additional process steps, soaking and subsequent drying, which can be very time-consuming regarding larger green bodies with very fine pores.

Finally, doping can be achieved by incorporation of solid nanosized particles into the pores of the green body prior to sintering. This can be achieved by electrophoretic impregnation, where nanosized particles are electrophoretically deposited inside the pore channels of a green body [9]. However, typically only several hundred microns to some millimetres of the green body can be impregnated homogeneously.

Since the size of the secondary phase incorporated into the green body is governed by the pore size of the green body and typically the functionality of a dopant within a glass is size dependent (e.g., ruby coloration, semi-conductor absorption), controlling the properties of the glass green bodies and especially their pore size distribution is of utmost importance [10]. Two requirements have to be fulfilled to enable manufacturing of doped glasses via powder shaping and sintering:

1. a sintering temperature sufficiently low to avoid crystallisation and to avoid evaporation of the dopant(s)
2. a pore size with a very narrow distribution adjusted to the optimum size of the functional secondary phase within the sintered glass (typically several nm to some ten nm)

One possible alternative is the sol–gel process [11], but the green density is strongly limited, resulting in high shrinkage during drying and sintering [12]. Even if very sophisticated and cost-intensive drying techniques are applied, cracking of large components can hardly be avoided. Thus sol–gel techniques are only suitable for small parts and coatings.

A suitable alternative is the compaction of nanoparticles to green bodies with adjusted pore size distribution. However, conventional shaping techniques known from ceramic processing cannot be easily adapted to the compaction of nanoparticles. Since the bulk density of nanopowders is very low, dry pressing is not well-suited for shaping of nanoparticles. Due to the high surface area of nanoparticles and the typically structural viscosity of suspensions and feedstocks, only very low green densities and poor homogeneity are achieved by shaping techniques using high-viscous feedstocks. Suspension based techniques seem to be much more promising, because a green density higher than the solids loading of the suspension can be reached at least from a well dispersed slip. However, due to the very low pore size of 5–50 nm that has to be achieved to allow an effective impregnation with functional secondary phases the velocity of body formation is very low in case of slip or pressure casting. The formation of a deposit from nanosized silica particles with 5 mm wall thickness by slip castings requires more than 7 h [13].

In contrast, deposition rate is independent of particle size for electrophoretic deposition (EPD) if the deposition is carried out perpendicularly to gravity. The phenomenon of electrophoresis is a well-known separation technique applied in chemical and biological analytics for decades. The first application of EPD as coating technique for highly loaded electrically conductive substrates was described in the middle of the last century. Nevertheless, only few applications have already been commercially realized, like the well-established electrophoretic painting and enamelling. A more recent industrial application of the EPD is the coating with ceramic insulators for aperture masks in TV. Generally, most applications of EPD in ceramic manufacturing by far are focussed on protective and functional coatings, with a focus on coatings for energy harvesting and conversion, bioactive coatings on implants and coatings for microelectronical applications [14]. Further applications of EPD are the manufacturing of functionally graded composites [15], the fabrication of layered composites by alternating EPD of different suspensions [16] and the production of fibre-reinforced structures by means of EPI of fibre performs [17]. Finally, the manufacturing of bulk ceramics from SiC, alumina, zirconia or piezoelectrica for MEMS [18] is of increasing interest. Even near-shaping of complex silica glass components is possible by EPD of powder mixtures of nanosized and bigger particles [19]. General reviews of the basic principles of EPD as well as of applications as ceramic coating and shaping technique are given in [20, 21].

A modification of conventional EPD from aqueous suspensions is the so-called membrane method where the deposit is formed on an ion permeable membrane [22]. Thus the incorporation of gas bubbles into the deposit as a result of the recombination of hydrogen and oxygen at the electrodes (due to the electrolytic decomposition of water above app. 2 V) can be avoided. The experimental setup is characterized by an ion permeable membrane that is located between the electrodes perpendicular to the moving direction of the particles during EPD. This method was successfully used for shaping different silica glass and ceramic components as well as microstructures that were deposited on a polyethersulfone membrane. Furthermore, green bodies consisting of nanosized silica particles could be shaped outstandingly fast by means of the membrane method. Thus a deposition rate of 10 mm/min was reached for nanosized OX50 with an applied electric field strength of only 10 V/cm. Furthermore, green density as well as pore size of electrophoretically deposited green bodies (OX50) could be tailored by adjusting the process parameters like e.g. the solids loading [23]. Compared to slip or pressure casting from the same highly stabilized suspension (pH 11, ζ-potential = –80 mV) with 16 vol.% solids content higher green densities were achieved (up to 50%TD) as well as a much better microstructural homogeneity [19]. As a result sintering of the EPD green bodies was finished at 1,320 °C whereas 1,450 °C were necessary to obtain a full densification of the slip cast sample [4].

Even though the manufacturing of complexly shaped and structured silica glass components via EPD and sintering is possible, there also is a strong demand for doped silica and multicomponent glasses. As described above, powder processing is mandatory to allow the production of glasses with of a broad variety of (new) doping materials. However, only a very few glass composition are commercially available as nanopowders. Thus doping of the glasses has to be achieved via impregnation of the green bodies with all the disadvantages described above. Thus a new method has to be found to prepare homogeneously doped silica and multicomponent glasses within one process step via powder shaping.

In this paper a modification of EPD, the so-called reactive EPD is used to produce homogeneously doped silica glasses, with doping and shaping being only one process step.

Experimental

Two nanosized fumed silica powders were used for the manufacturing of doped silica and multicomponent glasses, Aerosil OX50 and A380 (Degussa). While the mean particle size of OX50 is app. 40 nm, with a BET surface area of 50 m^2/g, the size of A380 particles is much smaller (8 nm) with a BET surface area of 380 m^2/g. The preparation of the suspensions was similar for each powder. The particles were added gradually to bidistilled water, after adding of an appropriate amount of tetramethylammonium hydroxide and the chosen amount of doping salts. Subsequently, the particles were dispersed by means of a dissolver (LDV1, PC Laborsysteme) with adjusted torque. The ζ-potential of the particles was measured by means of a Zetasizer 3000 (Malvern). Furthermore, rheological behaviour of the suspensions was characterised (HAAKE, Rheostress 1) and the specific conductivity (WTW, LF340) was measured. Thus an optimum pH of 11 could be determined for EPD for both powders. The solids content of the suspensions was 16 vol.% for OX50 and 10 vol.% for A380. Additionally, the sedimentation stability of suspensions was controlled by means of ATR (attenuated total reflection) spectroscopy using a germanium single crystal. Different soluble salts were used for EPR: $CoCl_2$, H_3BO_3, KOH and $AuCl_3$.

The membrane method was used for EPD as described above, which means that the electrophoresis cell was subdivided into two chambers by a porous ion-permeable polymer membrane or mould. Cellulose foils were used for simple experiments, whereas self-supporting polymethyl methacrylate (PMMA) moulds have to be used for the shaping of more complex or structured components. Such hydrophilic PMMA moulds with optimized porosity and pore size distribution can be produced by casting of emulsions of methyl methacrylate (MMA), water and PMMA particles with appropriate composition. One of the chambers of the EPD cell (confined by cathode and membrane) was filled with the suspension, the other one, the compensation chamber (confined by membrane and anode), with an electrolyte, typically bidistilled water with different amounts of TMAH. In some cases a salt was added to the compensation liquid. Since all particles carried a negative surface charge EPD was carried out under constant applied voltages towards the anode. Electric field strengths of 0.5–10 V/cm were applied and the deposition time adjusted to reach the specified wall thickness.

The principle of reactive EPD is based on the adsorption of the functional ions, added to the suspension, either on the surface of each particle or within the surrounding part of the electrochemical double layer. The specific structure of the double layer is schematically shown in Fig. 1, to allow a better understanding of the EPR process.

In this case a fixed inner layer of specifically adsorbed cations is chosen exemplary, with the charge decreasing linearly over the fixed layer. To guarantee charge balance, a second layer is build up on the fixed layer, consisting of both anions and cations, with an exponential decrease in charge towards the value of the surrounding liquid. Part of this diffuse layer is sheared off during motion of the particle. However, the fixed layer as well as a part of the diffuse layer remains on the surface of the particle during motion and thus will be found within the deposit after EPR. Adding soluble salts with functional ions to a suspension of nanosized silica particles with high specific surface area, results in an adsorption of a fraction of the functional ions on the particle, depending on pH solvent and specific adsorption. Thus these functional ions will be transported together with each single particle during reactive EPD and will be found within the green body with very homogeneous distribution.

After drying in air at room temperature (up to 24 h), green density was measured by means of Archimedes method. After dissolving of the green bodies in HF + HNO_3, the content of doping within the green body could be measured by ICP-AAS. Sintering of the silica glasses was carried out in air in a zone furnace. After sintering to fully dense glasses, the samples were ground and polished prior to UV/VIS spectroscopy (Lambda 35, Perkin Elmer).

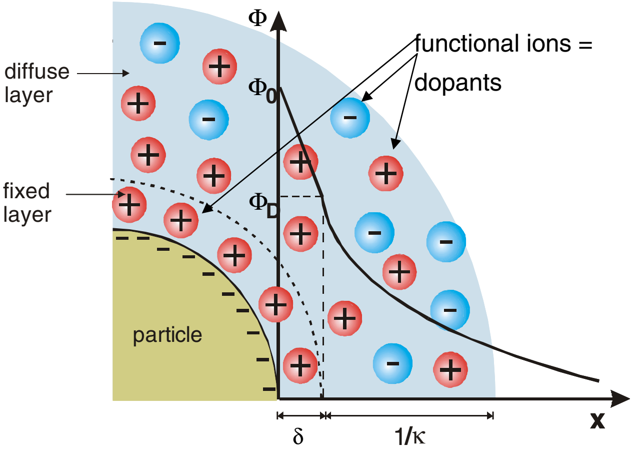

Fig. 1 Principle of reactive EPD, electrochemical double layer

Results and discussion

Doping with cations

The main goal of reactive EPD of (high silica) glasses was to enable shaping of complex glass components with a large variety of different functional dopings without additional processing steps, allowing the incorporation of non-toxic dopants with low temperature stability. To investigate the feasibility and limits of EPR, several systems were chosen, where the dopants are co-deposited either as cations or anions.

First of all, EPR with anions as dopants was investigated with Co^{2+} ions as model system, easily to determine within the sintered glass. Thus $CoCl_2$ was used as additive for suspensions containing 16 vol.% of OX50 each. After EPR the content of cobalt with the deposited green bodies was measured by means of AAS. The amount of cobalt within the green bodies after sintering was found to increase linearly with the concentration of $CoCl_2$ within the suspension (given in wt.% relating to the mass of OX50 within the suspension), used for EPR (Fig. 2). The yield is 0.53 ± 0.5, which means that app. 50% of the cobalt ions within the suspensions are deposited together with the silica particles and remain within the dried green body. Thus a tailored and predictable doping concentration can be achieved by adjusting the amount of $CoCl_2$ within the suspension, with linear interpolation in the concentration range investigated.

After sintering at 1,320 °C in air, a silica glass with homogeneous blue coloration was received, caused by the Co^{2+} ions incorporated into the network of the silica glass. No change in sintering temperature was observed compared to pure OX50. The transmission spectrum of a Co-doped silica glass, shaped from a suspension containing 0.1 wt.% of $CoCl_2$ by EPR is shown in Fig. 3. In comparison, the spectrum of a pure silica glass, shaped by EPD of a suspension of 16 vol.% OX50, is shown as well as the spectrum of a commercially available CoO doped silica glass. The low absolute transmission values result from the poor preparation of the glasses.

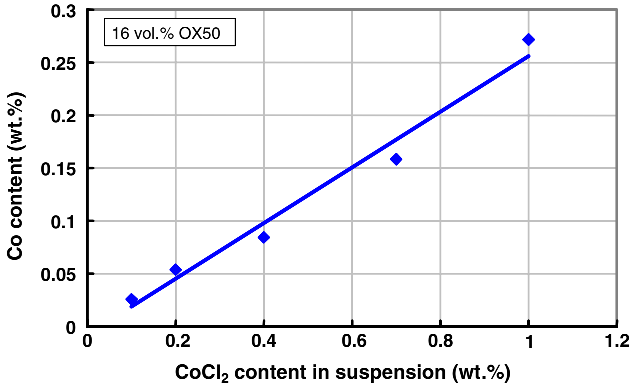

Fig. 2 Cobalt content within the green bodies after EPR of OX50 suspensions (16 vol.% each) with different concentrations of $CoCl_2$

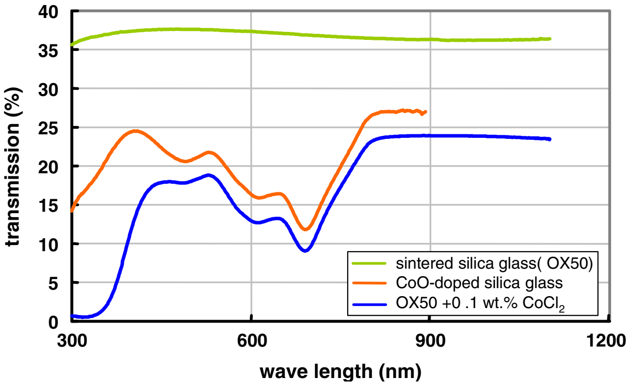

Fig. 3 UV/VIS transmission spectra of a cobalt doped silica glass, shaped by EPR, compared to a conventional CoO doped silica glass and a pure silica glass, shaped by EPD of OX50

With increasing content of $CoCl_2$ within the suspension and thus with increasing concentration of Co within the sintered glass an increase in the coefficient of absorption was observed, without any shift of the spectra concerning the absorption minima.

However, not only ion doping is of increased interest in manufacturing of doped (silica) glasses; also ruby red colouration is in the focus. Thus, the feasibility of EPR to produce homogeneously doped gold ruby silica glasses was investigated. Doping was achieved by EPR with $AuCl_3$. Since the colouration is dependent on the size of the gold clusters within the silica matrix here, which in turn is governed by the pore size of the green body, A380 (8 nm) was used as fumed silica, because finer pores could be achieved. The photograph on the left-hand side of Fig. 4 shows a gold ruby silica

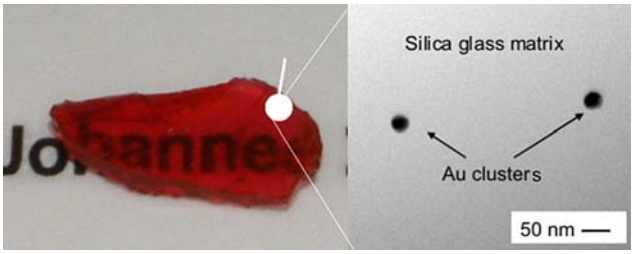

Fig. 4 Left-hand side: gold ruby silica glass, produced by EPR of A380 with $AuCl_3$ after sintering at 1,250 °C; right-hand side: TEM micrograph of nanosized gold clusters (30 nm) within the dense silica glass matrix

glass after sintering at 1,250 °C, shaped by reactive EPD. A very homogeneous red colouration was observed due to the nanosized clusters of metallic gold inside the fully densified silica glass matrix. The size of these clusters is app. 25–30 nm as shown in the TEM micrograph of the sintered gold ruby silica glass on the right-hand side of Fig. 4.

The spectra of two gold ruby silica glasses, produced by EPR of A380 with different concentrations of $AuCl_3$ are shown in Fig. 5. The typical spectral transmission of a gold ruby colouration can be seen, with the total transmission of the glass decreasing with the concentration of $AuCl_3$ within the suspension during EPR.

In contrast to the doping with cobalt the colouration is not caused by an incorporation of Co or rather CoO into the glass network but by the formation of metallic gold clusters within the glass matrix, indicating that different mechanisms of colouration can be achieved via EPR.

Doping with anions

The results shown above prove that homogeneous colouration of silica glasses via EPR is possible with predictably adjustable doping concentration, allowing the manufacturing of doped silica glasses with tailored transmission, without the risk of crystallisation. However, to increase the variety of dopants, a further decrease in sintering temperature is favourable, allowing the incorporation of semi-conducting dopants with low temperature stability.

Nevertheless, there are no appropriate glass powders commercially available that allow sintering at significantly lower temperatures than 1,250 °C without crystallisation. One promising solution is the doping of green bodies shaped with nanosized silica particles using additives reducing viscosity and sintering temperature. The incorporation of boron oxide into silica glass has the desired effect. Thus EPR with boric acid was investigated. There are two important differences compared to the results described above. First of all, the dopant is provided as anions within the suspensions. Besides, the amount of doping, necessary to achieve a distinct decrease in sintering temperature, is significantly higher. The amount of boron oxide within the green bodies shaped by reactive EPD, calculated from AAS measurements, is shown in Fig. 6 as a function of the concentration of boric acid within the suspensions with 16 vol.% OX50 each (dark curve, primary x-axis). As observed in EPR with cations, described above, a linear correlation was found between the amount of B_2O_3 within the deposit and the concentration of H_3BO_3 within the suspension. The yield was observed to be 0.50 ± 0.05, which means that app. 50 % of the BO_3^{3-} ions within the suspension were deposited by EPR and could be found in the dried green body. It is most remarkable that this is nearly equal to the value for Co found for EPR with $CoCl_2$, especially if it is taken into account, that the pH and thus the sign of the ζ-potential and the surface charge were the same. This means that app. the same amount of cations and anions are deposited by EPR at the same pH, which in turn means that after deposition the remaining part of the electrochemical double layer consists of an equivalent amount of cations and anions, resulting in a balanced charge.

Besides, the addition of boric acid to the compensation liquid resulted in a further increase in concentration of boron oxide within the deposit, as shown in

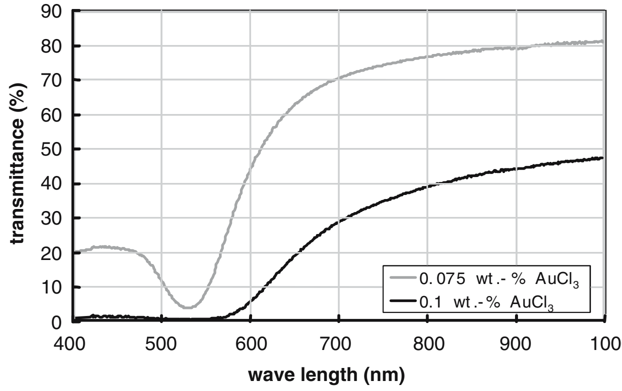

Fig. 5 UV/VIS transmission spectra of gold ruby silica glasses, shaped by EPR with different gold chloride concentrations

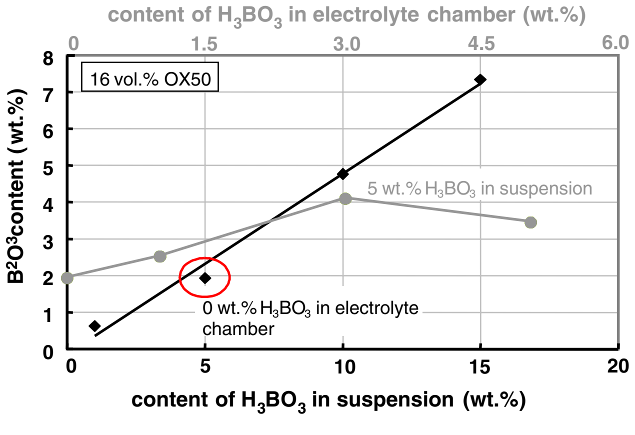

Fig. 6 Content of boron oxide within the green body as a function of the concentration of boric acid in the suspension (dark line, primary *x*-axis) and as a function of the H_3BO_3 concentration within the compensation liquid (light line, secondary *x*-axis) for a given content of 5 wt.% of H_3BO_3 in the suspension

Fig. 6. The light curve is associated to the EPR of a suspension with 5 wt.% of H_3BO_3, corresponding to the data point highlighted in the dark line. Different amounts of boric acid (secondary *x*-axis) were added here to the compensation liquid, resulting in a change in boron oxide concentration within the deposit. An increase of app. 100% of the boron oxide amount within the green body could be reached. This is mainly caused by the gradient of the chemical potential between the two chambers of the electrophoresis cell and the resulting electroosmotic flow, influenced by the concentration gradient. A similar approach with $CoCl_2$ was not successful due to the different sign of charge and the complexation of the Co ions.

The effect of boron oxide doping within the silica glass can clearly be seen in Fig. 7, where the sintering behaviour of a pure silica glass (OX50) is shown (dark dots) compared to a silica glass shaped by EPR with a concentration of 15 wt.% H_3BO_3 within the suspension (lighter squares). Due to the incorporation of boron oxide into the glass network a shift in sintering temperature from 1,320 °C to 1180 °C was observed. With lower content of boric acid within the suspension a correspondingly lower shift in sintering temperature was observed.

These results show that EPD is not only a method allowing doping with cations but also with anions, with considerable concentration. Again a linear interpolation is possible to adjust the doping concentration.

Co-doping with cations and anions

The results described above indicate that a homogeneous co-deposition of cations as well as anions should be possible by reactive EPD, because the yield was app. 50% for both species of ions over a large range of concentration. Thus incorporation of different functional ions in one EPR step was investigated as the key request to the incorporation of functional dopants with low temperature stability in glasses shaped from nanosized silica particles. First of all, a further reduction in sintering temperature was necessary. This can be achieved e.g., by co-doping of silica glass with boron oxide and K_2O, which basically is a multicomponent glass. By EPR of OX50, or any other fumed silica, with H_3BO_3 and KOH such a multicomponent glass can be produced via powder compaction and sintering at very low temperatures, as can be seen in Fig. 7.

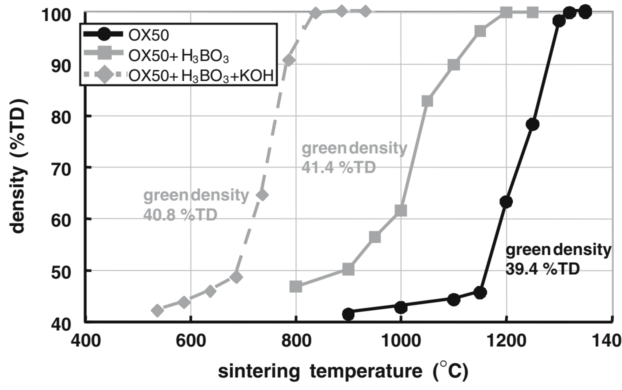

Fig. 7 Influence of EPR with boric acid and EPR with H_3BO_3 and KOH on the sintering behaviour of green bodies from OX50

The EPR of OX50 with H_3BO_3 and KOH resulted in a multicomponent glass, sintered to full density and transparency at 850 °C in air (light curve). Compared to pure OX50 this is a reduction in sintering temperature of 470 °C. Compared to the EPR boron oxide doped silica glass a further reduction of 330 °C was obtained. Thus a high silica glass could be produced by powder shaping and sintering, which is well-suited for the incorporation of functional (semi conductor) dopants.

Furthermore, the results prove that homogeneous co-doping with ions of different species is possible by means of reactive EPD, opening up a wide field of possible applications. However, if different salts are used for EPR concurrent adsorption of different cations and anions, respectively, has to be taken into account. A further investigation of the adsorption chemistry will be necessary then to allow the adjustment of dopants concentrations.

Conclusions

Using nanosized fumed silica particles, complexly shaped silica glasses can be shaped by EPD. However, due to a lack in suitable nanosized multicomponent glass powders and doped silica glass powders, manufacturing of such glasses has not been possible yet. In contrast, by means of reactive EPD homogeneously doped silica or multicomponent glasses can be produced from highly pure nanosized fumed silica particles, with shaping at room temperature and doping being only one process step. Soluble salts are used to provide the functional ions, resulting in a doping after EPR and sintering. Thus a large variety of possible doping materials exists. Since the doping ions are adsorbed within the electrochemical double layer surrounding each particle, a very homogeneous doping can be achieved with very short diffusion paths during heat treatment of the green body.

As could be shown in this paper, doping with cations is possible as well as with anions, because both species remain to a certain amount within the deposit after drying of the deposited green body. Thus silica glasses with a homogeneous blue colouration were fabricated by EPR with $CoCl_2$ and sintering at 1,320 °C, the coefficient of absorption being a function of the concentration of $CoCl_2$ in the suspension. A linear correlation between the amount of Co in the green body and $CoCl_2$ in the suspension allows predictable adjustment of the degree of doping of the sintered silica glass. Furthermore, EPR with $AuCl_3$ resulted in gold ruby silica glasses, with the total transmission being governed by the amount of $AuCl_3$ in the suspension.

Using H_3BO_3 as additive for EPR, the sintering temperature of the resulting glass could be decreased, again with linear correlation between the H_3BO_3 in the suspension and the amount of boron oxide within the green body. In contrast to the colouration described before, here the doping was achieved by EPR of anions. Remarkably, the yield was found to be nearly the same (app. 50%) independent of the fact that the doping was achieved via anions or cations. This suggests that the remaining part of the electrochemical double layer surrounding each particle after EPR and drying is comprised of app. The same amount of anions and cations.

Thus co-deposition of different materials should be possible. This was proven for the manufacturing of a multicomponent high silica glass by EPR of OX50 with H_3BO_3 and KOH. The resulting sintering temperature was 850 °C, which is a decrease of 470 °C compared to pure OX50. If the competing specific adsorption of different ions onto the surface of the particles or into the electrochemical double layer is taken into account even more complex systems can be co-deposited via EPR with predictable and tailored dopant concentration.

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