Original Paper

# Improved homogeneity of various glasses by gas film levitation[1)]

Achim Janke[2)] and Günther Heinz Frischat

Institut für Nichtmetallische Werkstoffe (Professur für Glas), Technische Universität Clausthal, Clausthal-Zellerfeld (Germany)

Heavy-metal fluoride glasses of the system $ZrF_4-BaF_2-LaF_3-AlF_3-NaF$ and soda−lime−silica glasses both from industrial and laboratory crucible production were processed by the gas film levitation technique. In this process the glass melt is suspended contactlessly on a thin gas film, avoiding any reaction with the crucible material. This prevents chemical contamination, surface defects and heterogeneous nucleation, which is especially advantageous for the preparation of specialty glasses. The overall homogeneity of the glasses was strongly improved, too, which was characterized quantitatively by the Christiansen-Shelyubskii method.

**Verbesserte Homogenität verschiedener Gläser durch Gasschicht-Levitation**

Fluoridgläser aus dem System $ZrF_4-BaF_2-LaF_3-AlF_3-NaF$ und Kalknatronsilicatgläser industrieller Produktion sowie aus der Tiegelherstellung wurden mit der Gaslevitationsmethode geschmolzen. Dabei schwebt der flüssige Glastropfen kontaktlos auf einer dünnen Gasschicht, wodurch jegliche Reaktion mit dem Tiegelmaterial vermieden wird. Dadurch werden chemische Verunreinigungen der Schmelze, die Ausbildung von Oberflächendefekten und eine mögliche heterogene Keimbildung verhindert, was besonders für die Herstellung von Spezialgläsern wichtig ist. Auch die Gesamthomogenität der Gläser wird stark verbessert, was quantitativ unter Einsatz der Christiansen-Shelyubskii-Methode verfolgt werden konnte.

## 1. Introduction

The preparation of glasses with appropriate optical characteristics requires a variety of additional homogenization techniques in order to reduce inhomogeneities in size and number even during fining. This is essential since quality problems of the glass adversely affect the optical properties. In general, glass technology provides a broad range of techniques, using chemical additions (e.g. $Na_2SO_4$), mechanical stirring (forced convection), gas bubbling or additional electrical heating [1]. These techniques permit the melting of optical glasses even of extreme compositions in acceptable quality.

When discussing inhomogeneity in glasses one usually means those spatial variations in composition which mass transfer can eventually remove. Most glasses are formed by heterogeneous reactions, in particular by the dissolution of some refractory constituents in melts formed by some of the other constituents. Often some of the earliest liquids to form differ considerably in density, viscosity and other properties, so that there can even be a gravity-induced segregation. Besides these inevitable sources of inhomogeneity for the bulk glass, there can be the formation of further inhomogeneities at the surface of the melt by evaporation and/or reaction with the atmosphere and by dissolution processes at the interface melt/refractory container. Platinum crucibles do not normally react with the melt to an extent that produces gross inhomogeneities. However, the tiny amounts of platinum that can dissolve sometimes lead to special problems, e.g. during laser or optical glass production [2], or they may act as sources for heterogeneous nucleation, specifically in the case of heavy-metal fluoride glasses [3].

Stresses caused by thermal treatment are not compositional inhomogeneities, even though they may result in a variation of optical properties. These stresses can mostly be removed simply by proper annealing. A number of further glass defects have to be considered, e.g. crystals, bubbles, stones, cords, which can occur both in the bulk and at the surface of the glass. When present, they also strongly influence the optical performance of the glass. Although these defects mostly do not fall into the category of inhomogeneity discussed above, their occurrence has to be prevented. The quality of e.g. fibers, sensors or lasers is of course greatly affected by such scattering centers.

A new possibility of improving the homogeneity of glasses in general is given by the gas film levitation technique, which has been applied recently especially to heavy-metal fluoride glasses [4 to 6]. This method is based on crucibleless melting on a thin gas film, utilizing the lubricating properties of this film formed by a gas stream through a porous membrane. The thickness of the gas film is typical several tens of micrometers,

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2) Now: Kaiserstein 21, D-97615 Marktredwitz.

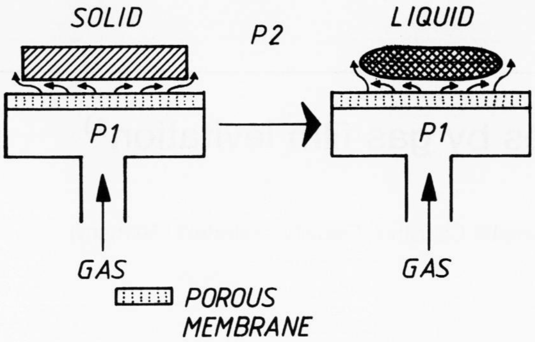


Figure 1. Principle of the glass film levitation method, horizontal levitator [6].

depending on geometry and membrane material and the kind of gas chosen. Typical glas flow rates across the membrane are about 1 l/min at room temperature. This inhibits any reaction between melt and crucible material. It is further supposed that, for example, a disc-shaped sample used during levitation can much more effectively be homogenized by convection currents than during melting in a crucible, where the edges remain nearly unaffected by these currents. This new technique is expected to have a special impact on the development of the heavy-metal fluoride specialty glasses, which are assumed to have potential as optical components such as ultra-low-loss waveguides, sensors or rare earth doped optical fibers, lasers and fiber lasers [7].

In the present study this new gas film levitation technique is applied to several silicate and heavy-metal fluoride glasses. The improvement of homogeneity is monitored by the Christiansen-Shelyubskii method, which has been shown to be a suitable technique both for industrial and laboratory glasses [8 and 9].

## 2. Experimental

### 2.1 Glasses

The soda–lime–silica glasses were commercial float glasses (Societa Italiana Vetro (SIV), San Salvo/Chieti (Italy)) and platinum crucible melted glasses with a batch close to that of the float glass. The melts were fined for 5 h at 1450 °C. After solidification the samples were tempered for 2 h at 570 °C in order to reduce the thermal stress.

Several heavy-metal fluoride glasses with compositions (in mol%) close to $53ZrF_4-20BaF_2-4LaF_3-4AlF_3-19NaF$ were prepared, basically determined by variations in their barium/sodium ratio. Raw materials from Merck, Darmstadt (Germany), were used. They were first dried at 130 °C for 15 h. The best choice for melting conditions, also in order to reduce evaporation, is given by

- a heating rate of 10 K/min and a final temperature of 400 °C,
- a heating rate of 30 K/min and a final temperature of 800 °C.

Melting was done in a platinum crucible in a nitrogen-flushed glove box (Labmaster 130, M. Braun, Garching (Germany)) using a furnace system with graphite susceptor. At 800 °C a fining step of 1 h seemed to be the optimum between homogenization and evaporation. Finally the melt was poured into a preheated aluminium mould (at 250 °C, below the temperature range of nucleation), solidified for 30 min with cooling of the glass to ambient temperature, resulting in disc-shaped samples with a diameter of 20 mm and a value for $T_g$ of 267 °C ± 3 K. Problems with the occurrence of a black phase were overcome by the addition of $InF_3$ as an in-situ oxidant (0.2 mol%) [10]. So far, no nucleating properties of $InF_3$ had been reported and an influence on homogeneity was not likely to occur.

### 2.2 Gas film levitation

Levitation generally provides possibilities of improved homogeneity and performance for the preparation of glasses on a laboratory scale. This technique permits the production of defect-reduced samples e.g. from ultrapure precursors. The premelted glass is suspended in this crucible-free method by electromagnetic, acoustic or aerodynamic effects, which prevents:

- chemical contamination;
- surface defects, and
- heterogeneous nucleation.

Under normal gravity conditions [11] most of these techniques show only limited potential. Moreover, the material has to be conductive or the levitation methods permit only the processing of small, spherical samples of a volume < 1 cm³. The gas film levitation technique, see a schematic in figure 1, on the other hand, has the most promising potential for the processing of larger specialty glass samples up to about 15 g in weight. This should especially permit the production of ultrapure and strongly defect-reduced glasses both in the bulk and at the surface. As presented, this type of levitation is based on the lubrication effect of a gas film several tens of micrometers thick, inhibiting direct contact between the melt and a porous membrane [6].

During processing, too strong oscillations at the surface of the melt can disturb the homogenization of the glass if the gas flow exceeds a critical value. In general, this is determined by the volume of the liquid and its characteristics, such as surface tension, density and viscosity. Thus, size and geometry of precursor materials depend on the kind of glass selected, as table 1 presents for the variety of samples discussed in this paper. The diameter defines the size of the sample, whereas its radius of curvature is determined by the melt properties and requires a specially adapted, preferably hemispherical-shaped porous membrane for the levitation process [6]. However, the strong oscillations mentioned do not occur during the processing of silicate melts; their viscosities are too high. In contrast, due to their reduced viscosities and increased densities, fluoride glasses suffer more from this effect. Therefore, a more precise control of the levitation parameters is necessary. Tables 2 and 3 summarize some of these technological conditions and a selection of materials for the glass melts processed.

Successful levitation of fluoride glasses is possible also for larger geometries up to 15 g in weight, e.g. discs or rods [5]. The horizontal levitator, however, can only be operated discontinuously, whereas the vertical levitator was developed to permit a continuous process for samples of circular shapes.

### 2.3 Characterization of homogeneity

The Christiansen-Shelyubskii method was used to monitor quantitatively the homogeneity. Crushed glass and an immersion liquid are filled into a heated spectrophotometer cell. This is penetrated by monochromatic laser light. Maximum transmission occurs exactly at the temperature at which the refractive indices of most of the glass grains and the liquid are identical, resulting in a Gaussian transmission curve. Both maximum transmission, $\tau_0$, and half-width value, $h$, determine the homogeneity factor, $\sigma$ [8 and 9], which represents the standard deviation of the refractive index of the grains. Improved homogeneity occurs at low $\sigma$ values. In order to make the results comparable, the following conditions were chosen:

- He/Ne laser with a wavelength of 633 nm,
- identical cell length (normally 5 mm),
- moderate heating rate near 0.3 K/min,
- identical granular fraction of 0.1 to 0.2 mm and 0.35 to 0.5 mm for fluoride and soda–lime–silica glasses, respectively,
- type of immersion liquid: tetrachloroethene for fluoride glasses, and chlorobenzene for soda–lime–silica glasses,
- identical transmission model.

## 3. Results and discussion

### 3.1 Soda–lime–silica glasses

As shown in figure 2, crucible-made soda–lime–silica glasses show poor homogeneity irrespective of additional technological efforts. Thus, homogenization by grinding of the batch components to a granular size below 100 µm is not very effective, see table 4. Crushing and remelting of the glasses is much better, which leads to strongly improved (transmission near 50%) but still unacceptable homogeneity compared to tank-made commercial glasses [9]. It has been shown earlier that homogeneous glasses result in half-width values $h < 1$ K [8]. Due to a change in the transmission model when going from homogeneous to inhomogeneous samples (i.e. maximum transmission $\tau_0 < 20\%$), the half-width, $h$, increases [8]. This can be seen by comparing the data of sample 3 with those of samples 1 and 2 of table 4. The $h$ values of samples 1 and 2 are increased by a factor of about 3. As figure 2 displays, levitation is a much more effective homogenization method. Of course, proper conditions, e.g. with respect to temperature, have to be chosen. Thus, the homogeneity of the sample levitated at 1300 °C is enhanced. However, going to a levitation process at 1450 °C gives an even better result, with $\tau_0 > 80\%$, see also table 4. Note that the half-widths, $h$, of samples 4 and 5 are increased, although sample 5 is very homogeneous. Since the amount of levitated material was small, the spectrophotometer cell length had to be reduced from 5 to 2 mm, which influenced the measuring conditions strongly. Nevertheless, the results obtained prove the efficiency of the levitation method even under these less ideal conditions.

It should also be noted that the maximum peak positions are shifted towards lower temperature (figure 2). Obviously this is due to a small surface evaporation loss of e.g. $Na_2O$ during the additional heat treatment. By this the structure of the glass is contracted and a property like the refractive index is influenced to some extend, too.

Table 1. Geometrical requirements and total mass for the levitation of the glasses discussed

| property | soda–lime–silica glass | heavy-metal fluoride glass |
|---|---|---|
| diameter in mm | 30 | 20 |
| radius of curvature in mm | 50 | 30 |
| total mass in g | 10 to 12 | 6 to 8 |

Table 2. Technological conditions for the levitation of glasses

| sample material (temperature) | gas | critical contamination |
|---|---|---|
| oxide glasses (1450 to 1500 °C) | air | moisture, dust |
| fluoride glasses (below 1000 °C) | inert gases (Ar, He, $N_2$) | oxygen, dust, moisture < 1 ppm |

Table 3. Selection of the materials used for critical components depending on the atmosphere

| processing atmosphere | diffusing membrane | high-temperature pressure chamber |
|---|---|---|
| air | $Al_2O_3$ | $Al_2O_3$ |
| fluoride-containing gases | graphite | glassy carbon |
| inert gases | $Al_2O_3$, graphite | $Al_2O_3$, graphite |

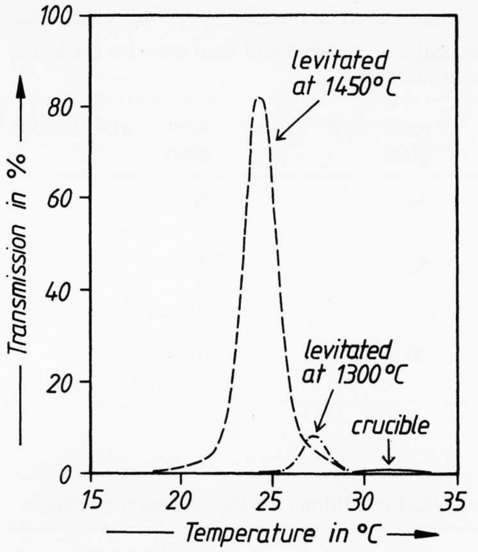


Figure 2. Christiansen-Shelyubskii transmission characteristics of levitated crucible-made soda–lime–silica glasses processed at different temperatures compared to the transmission of an otherwise identical precursor material.

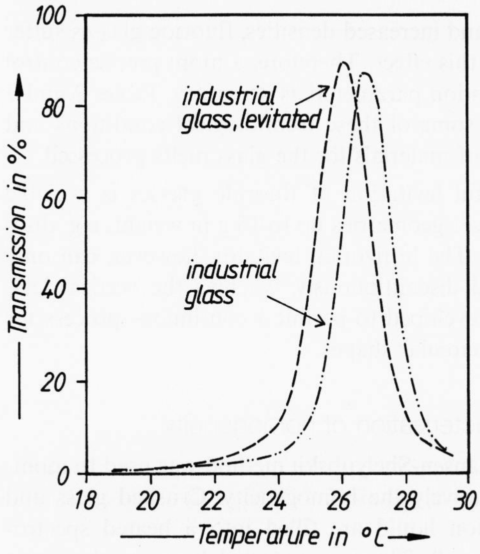


Figure 3. Christiansen-Shelyubskii transmission characteristics of a levitated industrial soda–lime–silica glass compared to the transmission of an otherwise identical precursor material.

Table 4. Christiansen data of crucible-made soda–lime–silica glasses and levitated counterparts

| sample | property | $\tau_0$ in % | $h$ in K | $\sigma$ |
|---|---|---|---|---|
| 1 | crucible, 3 h, 1450 °C | 0.9 ± 0.02 | 2.7 ± 0.1 | $1.8 \cdot 10^{-3} \pm 0.1 \cdot 10^{-3}$ |
| 2 | crucible, 3 h, 1450 °C particle size < 100 μm | 1.5 ± 0.03 | 2.8 ± 0.1 | $1.8 \cdot 10^{-3} \pm 0.1 \cdot 10^{-3}$ |
| 3 | 5 h, 1450 °C remelting | 48.5 ± 1.1 | 0.9 ± 0.04 | $2.4 \cdot 10^{-4} \pm 0.1 \cdot 10^{-4}$ |
| 4 | levitated, 2 h, 1300 °C | 8.0 ± 0.02 | 1.5 ± 0.1 | $7.3 \cdot 10^{-4} \pm 0.4 \cdot 10^{-4}$ |
| 5 | levitated, 3 h, 1450 °C | 82.4 ± 1.9 | 2.1 ± 0.1 | $3.0 \cdot 10^{-4} \pm 0.2 \cdot 10^{-4}$ |

Table 5 displays the results of a levitation treatment of industrial float glasses compared to the as-received sample. Since the amounts of the levitated materials were again insufficient, all homogeneity measurements had to be performed with 2 mm cells. Despite the increased half-widths the results show that – comparing samples 6 and 9 – the 1500 °C levitated glass has an enhanced maximum transmission. Here again, the peak positions of the samples levitated are shifted a little due to a change in surface $Na_2O$ concentration (figure 3).

## 3.2 Heavy-metal fluoride glasses

Heavy-metal fluoride glass melts have much lower viscosities than silicate-based glass melts. Thus, for example, the viscosity at a temperature of about 600 °C of melt compositions used here is <1 dPas, whereas the soda–lime–silica melt counterparts have viscosities at 1400 °C (a comparable temperature) of $10^2$ to $10^3$ dPas [12]. Therefore, homogenization and fining processes of fluoride glass melts are much easier. In accordance with that figure 4 displays that a crucible-made fluoride glass already has a maximum transmission of $\tau_0 \approx 65\,\%$, see also table 6. Levitation of a sample by remelting a pressed glass powder leads to a $\tau_0$ value of about 90 %, reaching the level of industrial silicate glasses on this laboratory scale. In this case a direct comparison of the temperature values of both curves presented is not possible, since the initial compositions of the two glasses were dissimilar, although showing a similar overall performance. Table 6 also displays enhanced half-widths again, in this case due to the fact that because of the limited sample material the fine-grained fraction between 0.1 to 0.2 mm had to be used for the Christiansen-Shelyubskii measurement. As has been shown earlier, such fractions are less favorable to reach optimum conditions [8]. Improved homogeneities for levitated

Table 5. Comparison of Christiansen data of industrial soda–lime–silica glasses and their levitated counterparts

| sample | property | $\tau_0$ in % | $h$ in K | $\sigma$ |
|---|---|---|---|---|
| 6 | float glass | 87.9 ± 1.8 | 1.8 ± 0.04 | $2.1 \cdot 10^{-4} \pm 0.09 \cdot 10^{-4}$ |
| 7 | levitated 3 h, 1450 °C | 87.7 ± 2.0 | 2.1 ± 0.1 | $2.4 \cdot 10^{-4} \pm 0.1 \cdot 10^{-4}$ |
| 8 | levitated 12 h, 1450 °C | 83.1 ± 1.9 | 2.1 ± 0.1 | $2.9 \cdot 10^{-4} \pm 0.2 \cdot 10^{-4}$ |
| 9 | levitated 3 h, 1500 °C | 90.0 ± 2.1 | 2.0 ± 0.1 | $2.1 \cdot 10^{-4} \pm 0.1 \cdot 10^{-4}$ |

Table 6. Comparison of Christiansen data of crucible-made and levitated heavy-metal fluoride glasses

| sample | property | $\tau_0$ in % | $h$ in K | $\sigma$ |
|---|---|---|---|---|
| 10 | crucible, 1 h, 800 °C | 66.5 ± 1.5 | 1.4 ± 0.1 | $2.9 \cdot 10^{-4} \pm 0.2 \cdot 10^{-4}$ |
| 11 | levitated, pressed from powders | 90.5 ± 2.1 | 2.2 ± 0.1 | $2.2 \cdot 10^{-4} \pm 0.1 \cdot 10^{-4}$ |
| 12 | levitated, rod material | 79.8 ± 1.8 | 2.2 ± 0.1 | $3.3 \cdot 10^{-4} \pm 0.2 \cdot 10^{-4}$ |

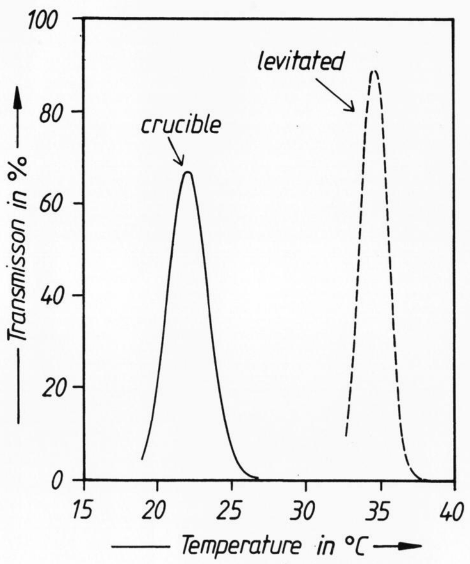


Figure 4. Christiansen-Shelyubskii transmission characteristics of a levitated heavy-metal fluoride glass compared to the transmission of a precursor material of somewhat deviating composition, however, similar overall performance.

fluoride glasses have been confirmed recently also by using laser scanning tomography and light scattering methods [6]. Sample 12 of table 6 finally shows that when using the vertical levitator, which permits the levitation of larger sample volumes, enhanced homogeneity can be achieved, too.

## 4. Conclusions

The gas film levitation technique provided improved homogeneity for all types of glasses examined in this work. This was especially the case when levitating crucible-made soda–lime–silica glasses. Industrial float glasses, on the other hand, are so homogeneous already in the as-received state that the improvements by levitation – although visible – are small. However, this new levitation melting technique is much more complicated than recently developed bubbling techniques for crucible melts [13]. Therefore this kind of homogenization route seems to be justified for silicate glasses only in special circumstances. Due to the low viscosity bubbling is not very effective for heavy-metal fluoride glasses [14], which means that the gas film levitation technique possibly is the only favorable means to produce ultrahomogeneous glasses, needed e.g. as preforms for sensor, laser or fiber applications. A major restriction of this new method still is an enhanced volatilization loss during levitation.

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Addresses of the authors:

G. H. Frischat
TU Clausthal, Institut f.
Nichtmetallische Werkstoffe
Zehntnerstraße 2a
D-38678 Clausthal-Zellerfeld

A. Janke
Kaiserstein 21
D-97615 Marktredwitz