Original Paper

Effect of TiO$_2$, ZrO$_2$ and ZnO addition on the hydrolytic durability, viscosity and crystallization behaviour of fibre glasses

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Glasses of the system Na$_2$O−K$_2$O−MgO−CaO−BaO−Al$_2$O$_3$−SiO$_2$−B$_2$O$_3$ with additions of TiO$_2$, ZrO$_2$ and ZnO were melted from the raw materials. The glasses were characterized with respect to their hydrolytic durabilities, the working ranges (difference of temperatures attributed to viscosities of 10^2 and 10^4 dPa s), the temperatures attributed to the working point ($\eta = 10^{3.5}$ dPa s), and the crystal growth velocities. In the most cases, the additions led to an increase in viscosity and to a slight decrease in the workability range. The crystal growth velocities decreased with the addition of TiO$_2$ and/or ZrO$_2$, while they increased if adding ZnO. The addition of ZnO or of TiO$_2$ and ZrO$_2$ resulted in better chemical durability.

1. Introduction

Glass fibres belong to the group of glassy mineral fibres and are widely used today. They can be divided into two groups, insulation glass fibres and micro glass fibres. The second group is used as liquid and respiration filter and also as ear protection [1 and 2].

Micro glass fibres are produced in several steps. At first, the raw materials are melted in a glass furnace and spheres or sticks are formed out of the melt. They are subsequently processed to fibre glass by a two stage fibrization process. Two typical procedures for the production of glass fibres are the drawing-blowing process and the centrifugal-blowing process [3 and 4].

In the respiratory tract, glass fibres can be precipitated. This is a problem for the production, processing and utilization of micro glass fibres. According to German law [5], glass fibres with diameters < 3 µm are supposed to pass into the human lung during respiration. Most of the inhaled fibres are shorter than 5 µm [6 and 7]. Solid particles can be removed out of the lungs through corrosion in the biological environment or transportation [8]. This is of special importance for insulation glass fibres which according to German law have to be biosoluble in the environment of the human lungs. For that purpose, in 1994, the algorithm of the "Kanzerogenitätsindex" (K_I) has been introduced. The K_I is used to evaluate the biostability of glassy fibres by means of the chemical composition. This index is given by the concentrations of sodium, potassium, boron, calcium, magnesium, barium and aluminium oxide:

$$K_I \equiv [\text{Na}_2\text{O}] + [\text{K}_2\text{O}] + [\text{B}_2\text{O}_3] + [\text{CaO}] + [\text{MgO}] + [\text{BaO}] - 2 \cdot [\text{Al}_2\text{O}_3]. \tag{1}$$

A glass fibre is not supposed to cause cancer if K_I is at least 40. It should be noted that this formula is highly ambiguous and might only be a rough measure of the biosolubility [4 and 8]. Nevertheless, besides highly Al$_2$O$_3$-containing fibres produced from natural rocks, most insulation glass fibres nowadays produced in Germany fulfil this requirement. By analogy, also many fibres used to produce micro glass fibres with diameters < 500 nm possess $K_I > 40$. For the blowing process used to produce the fibres, an as low as possible processing temperature is especially advantageous.

This paper reports on the effect of the chemical composition of fibre glasses, on their hydrolytic solubility, their viscosity and their crystallization behaviour. The base glass is a multi component glass whose composition is similar to glass fibres for filter application. This glass was modified through the addition of TiO$_2$, ZrO$_2$, TiO$_2$/ZrO$_2$ and ZnO to reach the following special requirements, which are higher than for insulation fibres. The K_I of the glasses should be ≥ 40 to accomplish the guideline TRGS 905 [5]. Furthermore the hydrolytic solubility should be small (hydrolytic class 3), because the glass fibres are in contact with water during their use [9 and 10]. The temperatures attributed to viscosities of 10^2 and 10^4 dPa s should differ by > 300 K. The crystal growth velocity of the glass has to be low; otherwise the production of fibres with the centrifugal-blowing process is not possible.

2. Experimental procedure

The glasses were melted from the reagent grade raw materials SiO$_2$, H$_3$BO$_3$, Al(OH)$_3$, Na$_2$CO$_3$, K$_2$CO$_3$, MgCO$_3$, BaCO$_3$, CaCO$_3$, TiO$_2$, ZrO$_2$ and ZnO. The compositions of the glasses are summarized in table 1. The batch was melted

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Table 1. Compositions of samples studied (in wt%)

sample	SiO_2	B_2O_3	Al_2O_3	Na_2O	K_2O	MgO	BaO	CaO	TiO_2	ZrO_2	ZnO
A	54.4	9.9	2.3	7.3	7.0	4.6	7.4	7.1	–	–	–
Ti1	53.2	9.8	2.2	7.8	7.8	4.6	6.7	6.9	1.0	–	–
Ti2	52.5	10.8	2.0	7.4	7.4	4.4	6.9	6.9	2.0	–	–
Ti3	52.6	9.7	2.2	7.4	7.8	4.5	6.5	6.5	2.8	–	–
Zr0.5	54.3	9.8	2.1	7.4	8.0	4.3	6.9	6.8	–	0.5	–
Zr1	54.1	9.8	2.1	7.3	7.1	4.7	7.0	6.8	–	1.1	–
Zr2	52.5	10.8	2.0	7.4	7.4	4.4	6.9	6.9	–	2.0	–
Zr3	52.8	9.7	2.2	7.2	7.0	4.3	7.0	6.8	–	3.1	–
Ti1Zr2	52.5	9.7	2.2	6.8	7.7	4.5	6.8	6.6	0.8	2.3	–
Ti1.5Zr1.5	52.8	9.7	2.3	6.2	7.9	4.2	7.2	6.7	1.5	1.6	–
Ti2Zr1	52.7	9.7	2.2	6.7	7.7	4.2	7.2	6.8	2.0	0.9	–
Zn1	53.2	9.8	2.3	8.7	8.0	4.5	6.1	6.7	–	–	1.0
Zn2	53.1	9.8	2.1	7.4	7.9	4.2	6.9	6.7	–	–	2.1
Zn3	52.4	9.7	2.2	7.9	7.9	4.3	6.2	6.6	–	–	2.8

in a platinum crucible at 1400 °C. Afterwards the raw melt was kept at 1500 °C for 30 min and then poured in water. In a second step, the quenched glass was remelted at 1500 °C for 45 min. The homogeneous melt was poured on a copper mould and annealed at 560 °C. Almost every composition was analysed using energy dispersive X-ray analysis (EDX).

Hydrolytic durability measurements were carried out with the grain fraction from 315 to 500 μm. In analogy to DIN/ISO 719 [11], 2 g of glass were treated with 50 ml deionized water at 98 °C. The solution was filtered and subsequently titrated with 0.01 mol/l hydrochloric acid against methyl red. In the following, this quantity of 0.01 mol/l hydrochloric acid is used as a measure of the hydrolytic durability. In order to determine viscosities at high temperatures, a rotary viscometer (VIS 403, Bähr (Germany)) was used. The results were referenced to a standard glass (DGG I, Deutsche Glastechnische Gesellschaft, Offenbach (Germany)). In order to determine crystal growth velocities, small glass samples were thermally treated in a gradient furnace and subsequently, the crystal sizes were determined using an optical microscope. First, the crystal growth velocities increased with increasing temperature, reached a maximum, decreased again and finally became zero. In the latter case, crystals were no longer detected using the procedure described above. The minimum temperature attributed to a crystal growth velocity of zero was assumed to be the liquidus temperature.

3. Results and discussion

3.1 Hydrolytic solubility

The hydrolytic durability of the base glass A was titrated with 1.23 ml hydrochloric acid and can be classified as hydrolytic class 4.

Figure 1 shows the hydrolytic durability (volume of 0.01 mol/l HCl of the titration) of the glasses with TiO_2 addition. Here, TiO_2 was added to the base glass while the ratio of the molar concentrations of the other oxides was kept constant. The glasses Ti1, Ti2 and Ti3 possess TiO_2 concentrations of 1, 2 and 3 wt%, respectively.

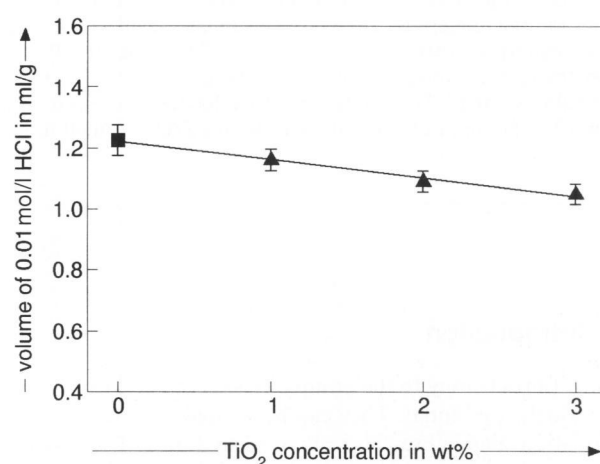A small but significant, within the limits of error, linear decrease of the quantity of HCl with increasing TiO_2 con-

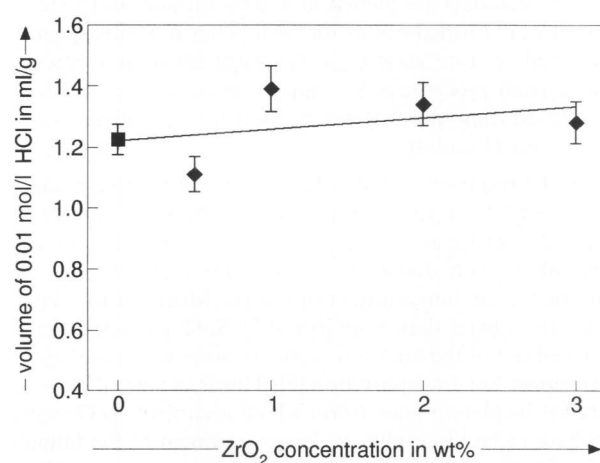Figure 1. Hydrolytic solubility of glasses containing TiO_2.

Figure 2. Hydrolytic solubility of glasses containing ZrO_2.

centration is observed. Hence, the addition of TiO_2 to the base glass A causes the improvement of the hydrolytic durability of the glasses [12 and 13].

In figure 2, the dependence of the hydrolytic durability is shown as a function of the ZrO_2 concentration. The glasses Zr0.5, Zr1, Zr2 and Zr3 possess a concentration of
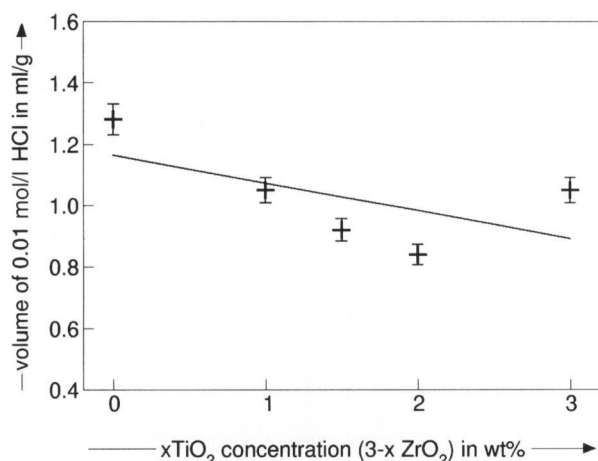
Figure 3. Hydrolytic solubility of glasses containing TiO₂ and ZrO₂.

Figure 4. Hydrolytic solubility of glasses containing ZnO.

0.5, 1, 2 and 3 wt% of ZrO₂, respectively. The addition of 0.5 ZrO₂ causes an improvement of the hydrolytic durability as the quantity of HCl decreased by about 0.12 ml. A further increase of the ZrO₂ concentration, however, leads to a decrease in the hydrolytic durability [14 and 15]. The volume of 0.01 mol/l HCl is even larger than the value of base glass A (1.23 ml).

Figure 3 shows the hydrolytic durability of glasses which contain both TiO₂ and ZrO₂. In the glasses Ti1Zr2, with 1 wt% TiO₂ and 2 wt% ZrO₂, Ti1.5Zr1.5, with 1.5 wt% TiO₂ and 1.5 wt% ZrO₂ and Ti2Zr1, with 2 wt% TiO₂ and 1 wt% ZrO₂, the sum of the TiO₂ and ZrO₂ concentrations was kept constant (3 wt%). The addition of TiO₂ and ZrO₂ to glass A leads to an increase in the hydrolytic durability. The glasses Ti3 (3 wt% TiO₂) and Zr3 (3 wt% ZrO₂) are included in further comparisons. The sample Zr3 shows the lowest hydrolytic durability (1.28 ml 0.01 mol/l HCl). By contrast, partial substitution of TiO₂ by ZrO₂ leads to an increase in the hydrolytic durability. While the volume 0.01 mol/l HCl of the sample Ti1Zr2 is the same as of Ti3 (1.05 ml), the hydrolytic durabilities of Ti1.5Zr1.5 (0.92 ml) and Ti2Zr1 (0.84 ml) are significantly better. These investigations show a mixing effect of TiO₂ and ZrO₂, which leads to a clear improvement of the hydrolytic durability.

Figure 4 presents the hydrolytic durability of glasses with ZnO addition. The glasses Zn1, Zn2 and Zn3 have a concentration of 1, 2 and 3 wt% ZnO, respectively. Figure 4 shows that the addition of ZnO causes a pronounced improvement of the hydrolytic durability of the glasses.

In summary, the glasses containing the oxides TiO₂, ZnO and the mixture of TiO₂/ZrO₂ show an increase of the hydrolytic durability. The improvement is in the following order: ZnO > TiO₂/ZrO₂ > TiO₂. On the other hand, the addition of ZrO₂ leads to a slight decrease in the hydrolytic durability.

3.2 Viscosities

The viscosity is a decisive property for the production of glass fibres. Two parameters were chosen for the evaluation and comparison of the viscosity measurements. The tem- -
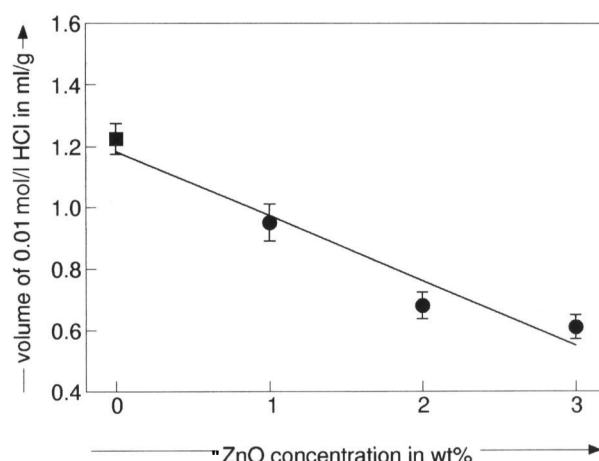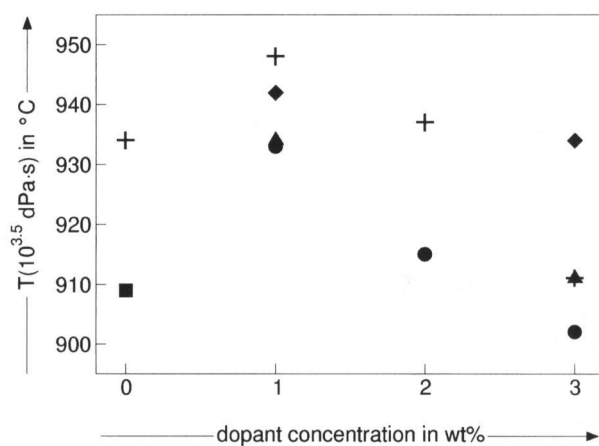

Figure 5. Temperature at $10^{3.5}$ dPa s as a function of the dopant concentration of (▲) TiO₂, (◆) ZrO₂, (●) ZnO, (+) x TiO₂ / (3-x) ZrO₂, and (■) base glass.

perature difference of η from 10^2 to 10^4 dPa s and the temperature at the working point lg η = $10^{3.5}$ dPa s. The first value indicates the suitability of the glass for mechanical processing and the second one gives a hint at which temperature the fibre glass can be well defibred.

Concerning glass A, the temperatures attributed to viscosities of 10^2 to 10^4 dPa s differed by 327 K and the temperature at η = $10^{3.5}$ dPa s is 909 °C. Figure 5 shows the temperature at $10^{3.5}$ dPa s as a function of the respective concentration of the added oxides. All additions lead to an increase in the temperature at the working point, which means the viscosity is higher. The maximum temperature is reached for the addition of 1 wt% of TiO₂, ZrO₂, TiO₂/ZrO₂ or ZnO. Further addition causes the decrease in the temperature, but in the most cases it is still larger than that of the base glass. The glass Ti1Zr2 (948 °C) has the highest viscosity, while Zn3 (902 °C) has the lowest viscosity. In figure 6, the temperature difference of 10^2 to 10^4 dPa s versus the concentration of the added oxide is shown. All measured samples, except Zn2, show a decrease in the temperature difference with the addition of the oxides, i.e. the glasses are shorter. The glass Zn2 (327 K) shows a similar workability range to glass A, but the temperature attributed to a viscosity of $10^{3.5}$ dPa s is 6 K higher. The further in-
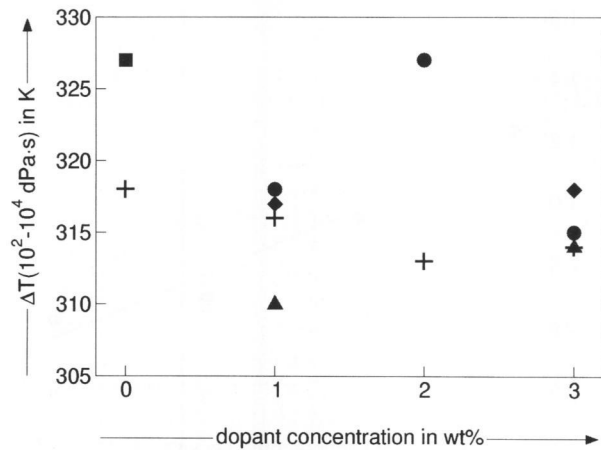
Figure 6. Temperature difference from 10^2 to 10^4 dPa s (workability range) as a function of the dopant concentration of (▲) TiO$_2$, (◆) ZrO$_2$, (●) ZnO, (+) x TiO$_2$ / (3-x) ZrO$_2$, and (■) base glass.
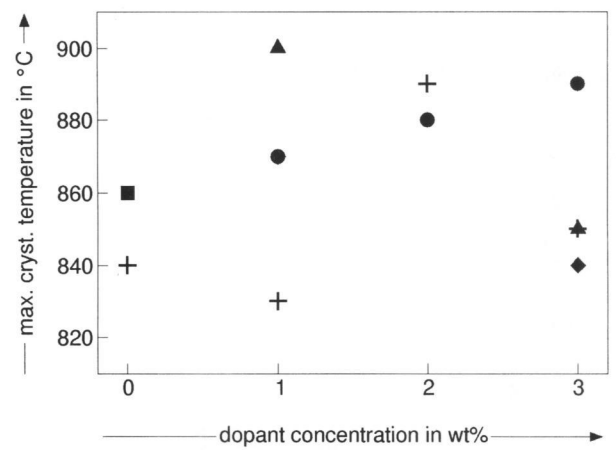

Figure 8. Temperature of the maximum crystallization as a function of the dopant concentration of (▲) TiO$_2$, (◆) ZrO$_2$, (●) ZnO, (+) x-TiO$_2$ / (3-x) ZrO$_2$, and (■) base glass.
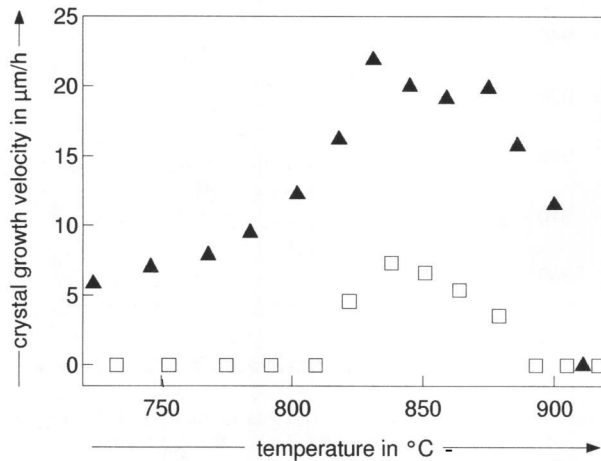

Figure 7. Crystal growth velocity of the glasses (▲) A and (□) Zr3.

Figure 9. Maximum crystal growth velocity as a function of the dopant concentration of (▲) TiO$_2$, (◆) ZrO$_2$, (●) ZnO, (+) x TiO$_2$ / (3-x) ZrO$_2$, and (■) base glass.

crease in the ZnO concentration to 3 wt% (sample Zn3) leads to a decrease in the temperature at $10^{3.5}$ dPa s (902 °C) and in the workability range ($\Delta T(\eta = 10^2$ to 10^4 dPa s) = 315 K).

3.3 Crystallization

The crystallization behaviour of the glasses is also important for the technical production of fibres. The glasses should not crystallize; otherwise the production of fibres with the centrifugal-blowing process is not possible. Figure 7 shows the crystallization behaviour of the samples A and Zr3. The maximum crystal growth velocity, the corresponding temperature and the liquidus temperature can be obtained from these crystallization curves. Glass A shows a maximum crystal growth velocity of 20 μm/h at 860 °C. This sample has a strong tendency to crystallization. The smallest maximum crystal growth velocity was observed in the glass Zr3 with 7 μm/h at 840 °C. The liquidus temperature is also different. While this temperature is 890 °C for sample Zr3, glass A has a 20 K higher liquidus temperature.
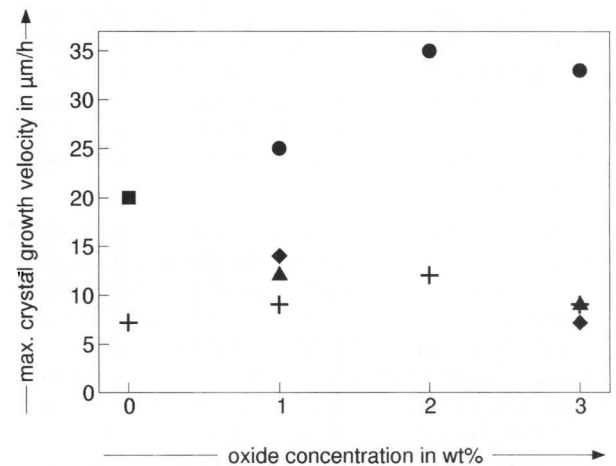
X-ray diffraction revealed that the heat treated sample Zn2 (880 °C, 180 h) contains diopside (CaMg(SiO$_3$)$_2$) (JCPDS 19-0239 [16]) as the only crystalline phase. The same crystalline phase was found in all samples; it has a characteristic appearance which can easily be identified by optical microscopy.

Figure 8 shows the maximum crystallization temperature of the glasses doped with TiO$_2$, ZrO$_2$, TiO$_2$/ZrO$_2$ or ZnO. The addition of 1 wt% TiO$_2$ causes an increase in this temperature of about 40 K to 900 °C. While further increasing the TiO$_2$ concentration, the temperature attributed to the maximum crystal growth velocity decreases. Glass Ti3 (850 °C) has a slightly lower maximum crystallization temperature than the base glass A. A similar behaviour can be observed for the addition of ZrO$_2$. Glass Zr1 shows maximum crystal growth velocity at a temperature of 870 °C and glass Zr3 of 840 °C. A linear increase in this temperature with the concentration is observed in the case of ZnO (glasses Zn1 to Zn3). The temperature increases by 10 K per wt% ZnO (Zn1: 870 °C, Zn2: 880 °C, Zn3: 890 °C). The glasses with TiO$_2$/ZrO$_2$ additions have a lower maximum crystallization temperature if the TiO$_2$ concentration is
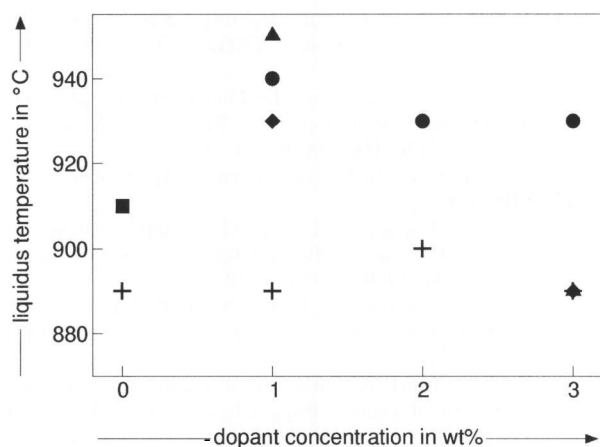
Figure 10. Liquidus temperature as a function of the dopant concentration of (▲) TiO_2, (◆) ZrO_2, (●) ZnO, (+) x TiO_2 / $(3-x)$ ZrO_2, and (■) base glass.

1 wt% (Ti1Zr2: 830 °C) and a higher temperature if the ZrO_2 concentration is 1 wt% (Ti2Zr1: 890 °C).

In figure 9, the maximum crystal growth velocity is shown as an effect of the concentration of the added oxides. An almost linear increase in the crystal growth velocity with the ZnO concentration is observed. Sample Zn3 has a crystal growth velocity of 33 μm/h, which is 13 μm/h more than the base glass A. All other additions lead to a clear decrease in the crystal growth velocity. The glass Zr3 with 3 wt% of ZrO_2 exhibits the lowest velocity (7 μm/h). Figure 10 presents the effect of the different additions to the base glass A (910 °C) on the liquidus temperatures. The liquidus temperature increases for the glasses with 1 wt% TiO_2, ZrO_2 or ZnO, while it decreases for the glass Ti1Zr2 (890 °C). The addition of 2 wt% ZnO results in a small decrease in the liqidus temperature (Zn2: 930 °C), which remains constant if the ZnO concentration is increased to 3 wt% (Zn3: 930 °C). The glasses with TiO_2 or ZrO_2 show smaller liquidus temperatures (Ti3 and Zr3: 890 °C) than the base glass A. Furthermore, the liquidus temperature increases from sample Ti1Zr2 to Ti2Zr1 (the glass Ti2Zr1 has a liquidus temperature of 900 °C).

3.4 General remarks

The composition of base glass A is that of micro glass fibres which are used in the production today. The composition was modified through additions of TiO_2, ZrO_2, TiO_2/ZrO_2 and ZnO. These additions affect the hydrolytic durability. While TiO_2 has only a slight effect and ZrO_2 causes even a decrease in the hydrolytic durability, additions of TiO_2/ZrO_2 or ZnO result in a significant increase. Another property which is affected by the addition of TiO_2, ZrO_2, TiO_2/ZrO_2 and ZnO is the viscosity. The temperature attributed to a viscosity of $10^{3.5}$ dPa s increases through the addition of TiO_2, ZrO_2, TiO_2/ZrO_2 or ZnO. This is a disadvantage for the economy of the glass fibre production. Furthermore, the temperature differences from 10^2 to 10^4 dPa s decrease for all additions, i.e. the glasses get shorter. The crystallization of the glasses increases notably through the addition of ZnO. The other additions, TiO_2 and ZrO_2, cause a decrease in the maximum crystal growth velocity.

Hydrolytic solubilities, characteristic temperatures as well as maximum crystal growth velocities are summarized in table 2.

With respect to the hydrolytic durability, ZnO has the largest effect of all additions studied. A hydrolytic class 3 can be reached. This is surprising, because according to [10], ZnO should have a minor effect, which e.g. should even be smaller than that of CaO. According to the literature (see e.g. [14 and 17]) the largest increase in the hydrolytic durability should be observed if adding ZrO_2. However, ZnO also increases the crystal growth velocity and furthermore the temperature attributed to a maximum crystal growth velocity, while the viscosity decreases. The difference in the temperature of maximum crystal growth velocity and the temperature attributed to a viscosity of $10^{3.5}$ dPa s decreases steadily from 63, 35 to 12 K for ZnO concentrations of 1, 2 and 3 mol% ZnO. Hence, the suitability for fibre production decreases with increasing ZnO concentration.

A hydrolytic class 3 can also be achieved by the addition of both ZrO_2 and TiO_2 (sample Ti2Zr1). Here, the temperature attributed to a viscosity of $10^{3.5}$ dPa s is 47 K above the maximum of the crystal growth velocity and 37 K above the

Table 2. Hydrolytic durability, temperature attributed to a viscosity of $10^{3.5}$ dPa s, temperature difference from 10^2 to 10^4 Pa s, maximum crystallization temperature, maximum crystal growth velocity and liquidus temperature of samples studied

sample	volume of 0.01 mol/l HCl in ml	temperature in °C	ΔT in K	maximum crystallization temperature in °C	maximum crystal growth velocity in μm/h	liquidus temperature in °C
A	1.23	909	327	860	20	910
Ti1	1.16	934	310	900	12	950
Ti2	1.09	–	–	–	–	–
Ti3	1.05	911	314	850	9	890
Zr0.5	1.11	–	–	–	–	–
Zr1	1.39	942	317	870	14	930
Zr2	1.34	–	–	–	–	–
Zr3	1.28	934	318	840	7	890
Ti1Zr2	1.05	948	316	830	9	890
Ti1.5Zr1.5	0.92	–	–	–	–	–
Ti2Zr1	0.84	937	313	890	12	900
Zn1	0.95	933	318	870	25	940
Zn2	0.68	915	327	880	35	930
Zn3	0.61	902	315	890	33	930

liquidus temperature. That means if the fibres are produced at the temperature where the viscosity is $10^{3.5}$ dPa s, the fibre cannot crystallize at all. With respect to these characteristic temperatures, this glass composition is even more suitable than the base glass A. In the latter, the liquidus temperature and the temperature where the viscosity is $10^{3.5}$ dPa s are the same within the limits of error.

All glasses studied have approximately the same workability range, which is always between 310 and 327 K. The chemical compositions of the glasses studied result in a K_I-value (see equation (1)) in the range of 38.5 to 40. However the glasses all possess the hydrolytic class 3 or 4 and hence have a fairly high chemical durability and are not supposed to dissolve in the human lungs within a short period of time. This points out that the K_I-value is not a suitable measure of the chemical solubility especially if components such as TiO$_2$, ZrO$_2$ and ZnO occur which are not included in the calculation of K_I.

In summary, the chemical durabilities of the alkali alkaline earth borosilicate glasses show a different behaviour with respect to the effect of additives in comparison to glasses without B$_2$O$_3$. Especially the glasses containing both TiO$_2$ and ZrO$_2$ are suitable for fibre production.

4. References

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