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Viscosity and liquidus temperature of quaternary glasses close to an eutectic composition in the CaO–MgO–Al_2O_3–SiO_2 system

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ABSTRACT

The thermal properties of the quaternary glass-forming CaO–MgO–Al_2O_3–SiO_2 system were evaluated. Different glass compositions with an expected liquidus temperature—the lowest temperature at which both the crystal phase and the melt are thermodynamically stable—below 1300 °C were melted from pure raw materials. Each oxide concentration did not deviate by more than ±3 mol% from that of the centre glass composition of 61.2 SiO_2, 26.3 CaO, 8.6 Al_2O_3 and 3.8 MgO. Viscosity data and the liquidus temperatures were determined, as well as the exact compositions of the respective glasses by X-ray fluorescence. It was of special interest for this study, whether small compositional changes have a stronger influence on T_{Liq} or T_3. The T_3-values, which are the temperatures attributed to a viscosity of 10^3 dPa s—showed a much larger variation and are in the range from 1263 to 1363 °C. An exchange of the network formers Al_2O_3 or SiO_2 by network modifiers CaO and MgO resulted in a decrease in viscosity. The effect of MgO was also shown by a comparison with glasses of similar compositions but without any MgO. The exchange between Al_2O_3 and SiO_2 did not show a significant difference in viscosity whereas the substitution of CaO by MgO increased the viscosity. The liquidus temperature varied between 1137 and 1192 °C—less than expected for a composition close to an eutectic system.

Introduction

For the glass industry, data of a large variety of glass properties are required to guarantee an error-free production process and the applicability within the field of interest. For the production of reinforcement fibres, such as those for polymer matrix composites, the knowledge of the liquidus temperature T_{Liq} and the temperature T_3, which is attributed to a melt viscosity of 10^3 dPa s are quite essential, because at this temperature, the glass melt is drawn to fibres [1–3]. In an industrial melt, crystallisation before and during the drawing needs to be avoided, because it affects the quality of the fibre or may even disrupt the drawing process. T_{Liq} is defined as the highest temperature at which crystals are thermodynamically

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stable in contact to the glass melt and hence both phases are in equilibrium [1, 4, 5]. Below this temperature, crystals might be precipitated, and in any case will not dissolve [1, 6]. Hence, T_{Liq} is a key data point for an effective fabrication of the glass products, in case of temperature fluctuations below T_{Liq} which might induce devitrification. Since T_{Liq} delivers a clear indication of the minimum possible melting and forming temperature, the energy costs can then be estimated as well [4].

The melting and fining conditions in glass furnaces are strongly affected by the viscosity η [7, 8]. The processing temperature (denoted as T_3), is commonly recognised as fibre-forming temperature [2]. Also the temperatures throughout the glass cooling schedule are predetermined by the viscosity [9].

The difference between T_3 and T_{Liq} is hereby of special importance: ΔT ($=T_3 - T_{\mathrm{Liq}}$) is often used as a first approximation of the tendency towards crystallisation during glass fibre drawing. Commercial experiences in the reinforcement fibre industry show that the forming temperature T_3 should be at least 50 K higher than T_{Liq}. If ΔT is chosen too low, the production might be disrupted due to devitrification, if chosen too high, the energy costs are raised unnecessarily, which is of course unprofitable for the commercial glass production [10].

The glass-forming ability of a melt is closely related to the viscosity at T_{liq}—the liquidus viscosity (η_{liq}) of the system: a low T_{liq} generally correlates with a high viscosity at the liquidus temperature, resulting in a large kinetic barrier to the atomic rearrangements required for crystallisation [11, 12]. Good glass-forming compositions are thus found close to eutectic compositions [11]. It is therefore important to have accurate knowledge of phase equilibrium diagrams for the glass-forming systems of commercial interest.

Particularly in multicomponent systems, small composition changes can cause dramatic changes in the liquidus temperature [4, 6]. Veit et al. [5] reported that compositional changes within the CaO–MgO–Al_2O_3–SiO_2—glass melt even smaller than 3 wt% may result in shifts of T_{Liq} by more than 20 K, causing a huge effect on ΔT as well.

For the present work, glass compositions in the quaternary system CaO–MgO–Al_2O_3–SiO_2 have been prepared and characterised. The region of interest was chosen within a range attributed to the lowest liquidus temperatures according to Figs. 3.318 and 3.319 of Ref. [13]. At these compositions, T_{Liq} is smaller than 1300 °C and hence comparatively low. These glass compositions are favourable because relatively low melting temperatures were the goal of this study which would enable an energy and environmentally advantageous production [14].

The invariant composition with an T_{Liq} of 1130 °C has, according to Koch et al., a wt% composition of 22.0 CaO, 3.9 MgO 11.6 Al_2O_3, 62.5 SiO_2 (which is in mol% 23.88 CaO, 5.89 MgO, 6.92 Al_2O_3, 63.31 SiO_2). Since T_{Liq} might vary strongly if the composition is changed slightly, a composition range next to this invariant point was chosen: 23.9–28.6 mol% CaO, 2.7–5.0 mol% MgO, 7.6–9.6 mol% Al_2O_3 and 59–63.4 mol% SiO_2. This is highly advantageous, because commercially produced glasses occasionally show slight compositional changes and thus choosing a composition at the eutectic point might save heating energy, but it simultaneously increases the risks of disturbances and interruption during the production process: if the variation of T_{Liq} is too high in case of small composition changes and exceeds the drawing temperature, crystallisation might occur. Therefore, not only the chosen composition itself is of interest, but also the properties in the composition range around it. This is why it was of interest for this study, whether small compositional changes have a stronger influence on T_3 or T_{Liq}, especially regarding the overall impact on ΔT. Also the effect of the mixed alkaline earth (CaO and MgO) on the viscosity should be determined.

Altogether 28 glasses near the eutectic composition with the lowest liquidus temperature of 1130 °C have been melted and characterised [15]. The exact chemical composition as well as the liquidus temperature was determined and the temperature at a viscosity of 10^3 dPa s was derived from the viscosity curves for each glass composition. Furthermore, these properties were compared with those of glasses without MgO from Ref. [16].

Experimental procedure

The chemical compositions of the 28 glasses are summarised in Table 1. The used raw materials were pure quartz of grain size C, $CaCO_3$ and $Al(OH)_3$ and $4MgCO_3 \cdot Mg(OH)_2 \cdot 5\,H_2O$ (all Merck AG). Each oxide concentration does not fluctuate by more than ±3 mol% from that of the centre glass mol% composition 61.2 SiO_2, 26.3 CaO, 8.6 Al_2O_3 and 3.8 MgO.

Table 1 Chemical compositions according to XRF-values and the nominal composition of glasses in mol%

Glass	Nominal compositions				XRF-results normalised				BO/T
	SiO_2 (mol%)	CaO (mol%)	Al_2O_3 (mol%)	MgO (mol%)	SiO_2 (mol%)	CaO (mol%)	Al_2O_3 (mol%)	MgO (mol%)	
1	60.5	27.4	8.8	3.3	60.9	27.0	8.9	3.2	3.46
2	62.3	25.3	9.1	3.3	62.6	24.8	9.3	3.4	3.53
3	61.2	26.3	8.6	3.8	61.7	25.7	8.8	3.9	3.48
4	61.2	25.2	9.1	4.4	61.6	24.5	9.2	4.7	3.50
5	59.8	25.6	9.6	5.0	60.2	24.9	9.6	5.4	3.48
6	60.1	27.3	8.2	4.4	60.2	26.7	8.3	4.8	3.39
7	59.9	28.6	8.9	2.7	60.6	27.9	9.0	2.5	3.46
8	62.5	27.1	7.7	2.7	63.1	26.4	7.8	2.7	3.46
9	59.3	28.1	7.6	4.9	59.9	27.3	7.8	5.0	3.35
10	61.7	25.8	8.1	4.4	62.4	25.2	8.3	4.2	3.47
11	61.9	26.7	8.2	3.3	62.8	25.8	8.3	3.2	3.48
12	60.5	26.0	9.1	4.4	60.7	25.5	9.2	4.6	3.47
13	61.3	27.3	8.2	3.3	61.7	26.6	8.3	3.5	3.44
14	62.3	25.3	9.1	3.3	63.0	24.7	9.2	3.1	3.55
15	61.9	25.1	8.6	4.4	61.8	24.4	8.6	5.2	3.47
16	61.3	28.4	7.7	2.7	61.8	27.9	7.8	2.5	3.42
17	63.4	24.3	9.5	2.7	63.6	23.7	9.6	3.1	3.58
18	59.0	28.2	7.8	4.9	58.6	27.4	7.9	6.1	3.31
19	60.3	27.2	8.1	4.4	59.8	27.5	8.0	4.6	3.36
20	62.1	25.3	7.6	4.9	63.0	24.8	7.8	4.4	3.46
21	61.3	24.2	9.6	5.0	62.5	23.8	9.7	4.0	3.56
22	63.3	24.3	9.6	2.7	64.6	23.6	9.8	2.1	3.62
23	60.7	26.9	9.1	3.3	60.9	25.9	9.2	4.0	3.48
24	62.5	24.0	8.5	5.0	63.0	23.6	8.7	4.7	3.51
25	60.2	27.5	9.6	2.7	60.3	26.4	9.7	3.6	3.49
26	59.3	28.1	7.6	4.9	59.9	27.2	7.8	5.1	3.35
27	61.9	25.1	8.6	4.4	62.6	24.2	8.8	4.4	3.50
28	61.3	26.3	8.6	3.8	61.4	25.8	8.7	4	3.46

The glasses 26, 27 and 28 had identical compositions as the glasses 9, 15 and 3, respectively, to check the reproducibility. The glass melt of 300 g was prepared from pure raw materials and then mixed by manual shaking.

A portion of the weighed raw materials was filled into a platinum crucible and heated up in a furnace with $MoSi_2$ heating elements until the major part of carbon dioxide was evaporated. Then, the next portion of the raw materials was added and the temperature was increased to 1590 °C and held for another 2 h.

To achieve comparatively rapid cooling, the melt was cast in 10 l of cold water and subsequently dried at 120 °C to improve the glass homogeneity. Afterwards, the glass was melted at a temperature of 1600 °C again, kept for 3 h, and finally cast on heat resistant steel (AL7) moulds spray coated with boron nitride and preheated to 600 °C. The crucible with the residual, adherent glass was reheated and cast into the second mould. After casting, the glass was transferred to a muffle furnace preheated to a temperature in the range from 775 to 805 °C, depending on the glass composition, slightly above the glass transition temperature, T_g. This cooling procedure was supplied to all glasses, and hence a direct comparison of densities and T_g is facilitated although the cooling rate might have a slight effect on the glass properties [17].

The compositions of all samples were determined using X-ray fluorescence (XRF) with a PANalytical MagixPro (4 kW Rh Tube, Kassel, Germany).

The glass transition temperatures T_g were determined via dilatometry in the temperature range from 200 to 900 °C using a heating rate of 5 K min^{-1} (dilatometer DIL 402 PC, NETZSCH Gerätebau GmbH, Germany). Cylindrical samples with length of around 20 mm and a diameter of 8 mm were drilled out of the first cast glass bulk.

The viscosity was determined via rotation-viscometry (Bähr VIS 403). The data were analysed by fitting the data points with polynomials using the software Origin 8.0 (OriginLab, Northampton, MA, USA) in order to obtain T_3. In this test, the torque required to maintain a preset rotational frequency of a cylindrical spindle inserted in a platinum crucible (containing exactly 13.8 cm^3 of glass) was measured as a function of the temperature. Two runs at 250 and 10 rotations per minute were performed for each composition. From this torque, the corresponding viscosity was calculated.

The viscometer was calibrated using a DGG standard glass and was also tested with Advantex®, a registered trademark of Owens Corning which was used under license. The temperature accuracy of the viscometer was given with ±0.1 K. The measured T_3 of Advantex® was between 1170 and 1177 °C in those tests and corresponds very well with the theoretical value of 1173 °C. In some more experiments with Advantex®, it was found that a change in volume of up to 0.5 cm^3 did not affect the T_3—determination by more than 1 K, indicating this systematic error is minimal. Since the investigated glasses are slowly crystallising glasses, a shift of viscosities due to small crystals within the melt can be ruled out. Overall, a maximum error of ±6 K is expected.

For the determination of T_{Liq} (following the ASTM standard procedure C829-81 [18]), crushed glass with a grain size smaller than 850 µm was filled into a platinum boat 250 mm in length and 10 mm in width. The platinum boat was then put into an Orton tubular furnace with 8 built-in thermo-couples for temperature surveillance and remelted at 1500 °C for 1 h to reduce gas bubbles which might affect the interpretation of results. Afterwards, the temperature was reduced to the range of interest and held for 24 h to induce crystallisation within the glass melt. Subsequently, the position of the crystals was studied using an optical microscope. The position in the boat and its corresponding annealing temperature was determined, where the crystals are found—going from high to low temperatures and is then attributed to the temperature which corresponds to T_{Liq}.

To ascertain the correctness and precision of the gradient furnace, a Standard Reference Glass (NIST 1416) from the National Institute of Glasses and Technology for the calibration of gradient furnaces was tested. This glass has a theoretical T_{Liq} of 1147 ± 4 °C. The experimental results of 1145 and 1142 °C correlate well with the theoretical value, demonstrating the right temperature regime within the used gradient furnace. Then, around 50 trials with glasses of a similar composition to the tested glasses and a theoretical T_{Liq} of 1220 °C were performed in the gradient furnace to test the repeatability of the measurement method. The values varied between 1214 and 1223 °C with a mean value of 1218.7 °C and a standard deviation of 2.7 K for this glass trial. Under the assumption that the values of the results are normally distributed, the measurement uncertainty is ±7 K at 3 SIGMA.

Results and discussion

Chemical composition, XRF

In Table 1, the nominal and the glass compositions determined by X-ray fluorescence (XRF) are summarised. The XRF-values added up to at least 99.74 wt% (indicating a very low amount of tramps) and have been normalised to 100 mol% for better comparison. In the following, the normalised XRF—data will be used for further correlations with the thermal properties.

In all samples, a shift of 0.4–1.1 mol% of the calcium oxide values from the intended CaO concentration was noticed. The higher CaO concentration mostly caused a decrease in the SiO_2 and MgO concentrations, whereas Al_2O_3 showed always a similar deviation of around 0.1 mol%.

The glasses 26, 27 and 28 had the same chemical compositions as the glasses 9, 15 and 3, respectively, to check the reproducibility. The glasses 9 and 26 were very similar and are thus comparable with each other. But glass set 27 and 15 and glass duo 3 and 28 show shifts within the MgO and SiO_2 concentrations of 0.8 and 0.2 mol%, respectively. Hence, the comparability is lower.

In Fig. 1, the analytically measured compositions (XRF) are illustrated in a 3D quaternary diagram,

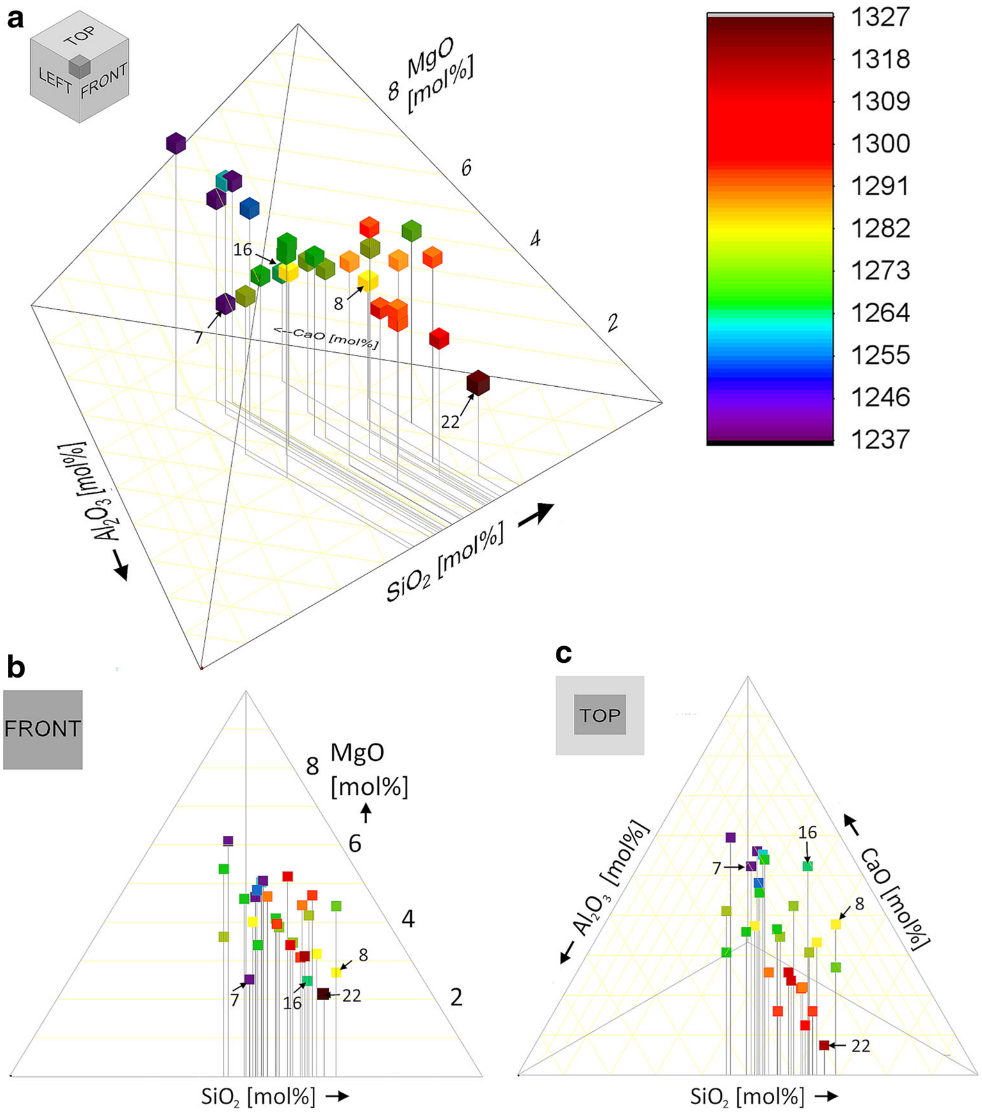

Figure 1 Temperature T_3 at a viscosity of 10^3 dPa s as a function of the composition (mol%) in a 3D phase diagram, with view from *side* (**a**), *front* (**b**) and *top* (**c**).

which is displayed from different angles for visualisation and better understanding.

Glass transition temperatures T_g

The glass transition temperatures, T_g, of the glasses are listed in Table 2. The transition temperatures of these 28 glasses vary between 754 and 783 ± 3 °C. It is well known that the relaxation times of glasses are only a few minutes at T_g [19, 20]. Also, the residual stresses in the glasses are gradually eliminated with increasing annealing time or temperature. Since all T_g values are lower than 800 °C, the right cooling temperature of the cooling furnace has been chosen and the glasses are relaxed.

The T_g values of the glasses 9 and 26 with almost identical compositions are 762 and 758 °C, respectively. Due to the limitations of the T_g-calculation with the tangent method in the applied analysis program, an error of ±3 K has to be taken into account. Hence, the results can be treated as identical values. Also the samples with identical compositions, 27 (765 °C) and 28 (771 °C), show only small deviations of 3 and 2 K from the corresponding original glasses 15 (762 °C) and 3 (773 °C), respectively. This can easily be explained by the analytical error of the tangent method when using the evaluation software.

In Fig. 3, the obtained T_g values are illustrated as function of the number of bridging oxygen per tetrahedron.

All glasses are peralkaline compositions, i.e. they have a ratio $(MgO + CaO)/Al_2O_3$ larger than 1. Hence, all tested samples contain network modifier

Table 2 Measured glass transition temperatures (T_g), processing temperatures (T_3)—and liquidus temperatures (T_{liq}) of the studied glasses

Glass	T_g (°C)	T_3 (°C)	T_{liq} (°C)	ΔT (K)
1	771	1269	1140	129
2	775	1301	1147	154
3	773	1277	1138	139
4	771	1286	1147	139
5	766	1269	1192	77
6	765	1254	1170	84
7	770	1238	1158	80
8	769	1282	1155	127
9	762	1258	1165	93
10	763	1278	1140	138
11	774	1280	1150	130
12	770	1273	1158	115
13	760	1275	1150	125
14	777	1298	1151	147
15	762	1294	1140	154
16	765	1266	1175	91
17	779	1308	1163	145
18	755	1241	1176	65
19	754	1237	1164	73
20	766	1268	1161	107
21	767	1294	1144	150
22	783	1327	1165	162
23	771	1280	1153	127
24	767	1296	1158	138
25	768	1278	1150	128
26	758	1240	1169	71
27	765	1286	1165	121
28	771	1271	1142	129
MIN	*754*	*1237*	*1138*	*65*
MAX	*783*	*1327*	*1192*	*162*

concentrations which are high enough to compensate the negative charge of the $[AlO_4]^-$ tetrahedra, and therefore aluminium oxide is built into the network as a network former, i.e. in fourfold coordination. When all $[AlO_4]^-$ tetrahedra are charge compensated by the network modifiers Ca^{2+}-ions or Mg^{2+}-ions, any excess Ca^{2+} and Mg^{2+} form non-bridging oxygen (NBO) sites and hence decrease the number of Si–O–Si bridges and therefore the number of bridging oxygen per tetrahedron (BO/T) [21]. This means, the higher the concentration of network modifier is, the larger is the number of non-bridging oxygen sites and the lower is the number of bridging oxygen per tetrahedron (BO/T) and the more pronounced is the weakening of the glass structure. Obviously higher concentrations of network modifiers decrease the transition temperature. Also in the comparison with glasses from Ref. [16], where glasses with similar compositions but without MgO were characterised, the slope is clearly visible. It is interesting to notice that the distribution of the T_g—values in the present paper is obviously broader than in the glasses which do not contain MgO.

The temperature T_3 at which the viscosity is 10^3 dPa s

In Table 2, the results for T_3 are summarised. It is obvious, that the comparatively small changes in the chemical composition are able to cause a huge variation of the temperature at which the viscosity is 10^3 dPa s and thus also of the working temperatures. This is a possible threat for ensuring a smooth process. The data show variations between 1237 °C (glass 19) to 1327 °C (glass 22), i.e. by 90 K, even though glasses with only small changes in the composition were studied. All viscosity curves had similar slopes showing that all glasses in this composition range have similar (temperature dependent) activation energies.

In Fig. 1, the T_3-temperatures of the glasses are presented as a function of the determined XRF-composition in a ternary phase diagram for better visualisation.

The colour code for the temperatures varies from the lowest value of T_3 for glass 19 with 1237 °C (violet) and the highest glass fibre-forming temperature at a viscosity of 10^3 dPa s for composition 22 with 1327 °C (dark red). This colouration is a guide for the eye.

Influence of the components

From the top view in Fig. 1, the effect of the calcium oxide concentration on the viscosity of the glass melt is apparent. The higher the CaO concentration in the glass melt is, the lower is the temperature, attributed to a melt viscosity of 10^3 dPa s: the highest T_3-temperature, that of glass 22 (dark red-bottom of picture) with 1327 °C had a CaO concentration of only 23.5 mol%, whereas the glass 7 (violet—top of picture) with the lowest T_3 had a CaO concentration of 27.9 mol%. Moreover, the colouring between those two extrema is following the rainbow colouring of the legend with rising CaO concentration.

Furthermore, T_3 increases with higher SiO_2 concentrations. This is also clearly visible in Fig. 2. An

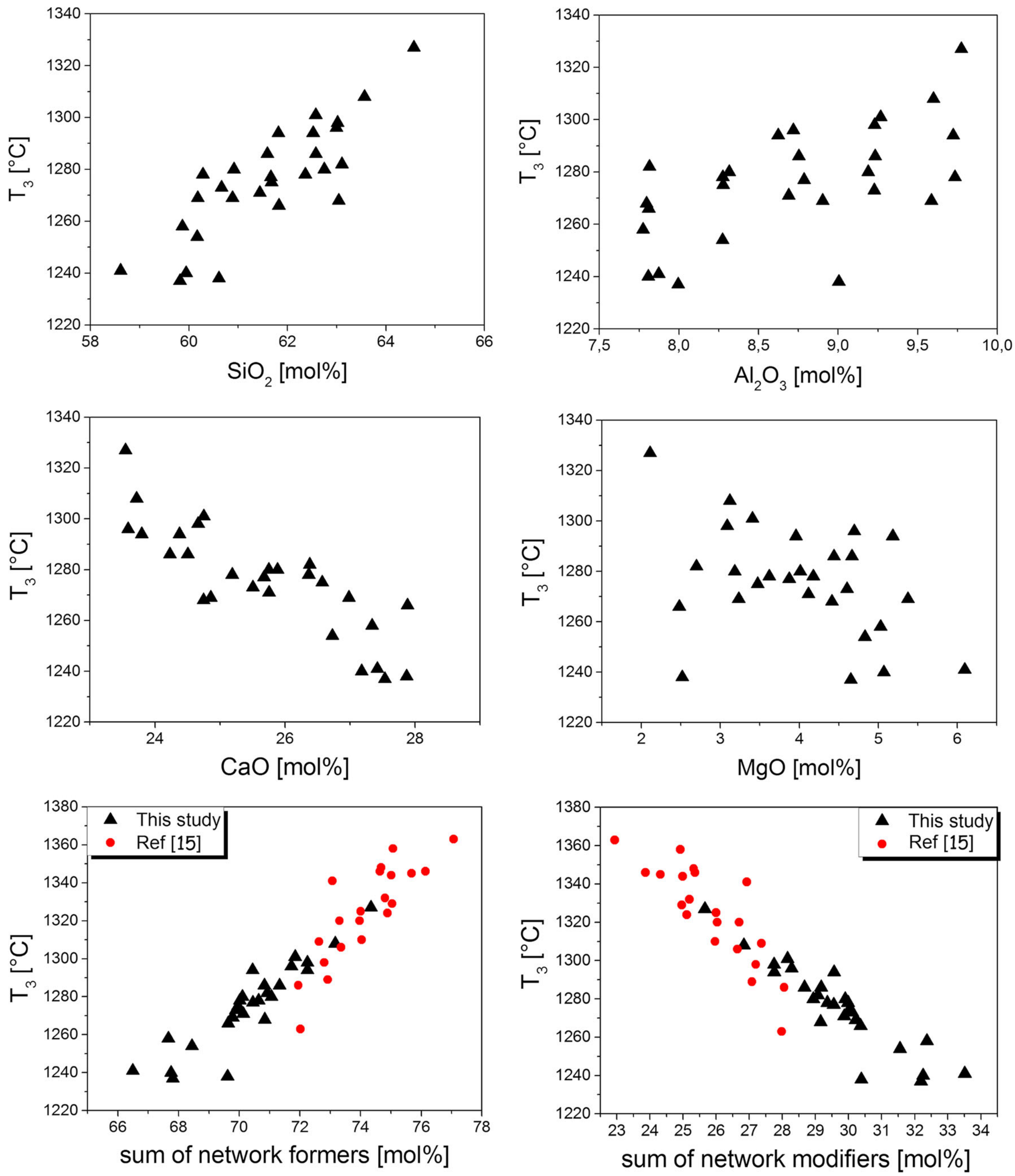

Figure 2 T_3 as function of oxide concentrations.

increasing Al_2O_3 concentration does not seem to affect T_3 significantly. Those results are correlating with Ref. [16] where ternary $CaO–Al_2O_3–SiO_2$ glasses are described, i.e. without MgO and have been described in the literature as well [17].

As shown in Fig. 3, there is a clear correlation between the BO/T and the T_3 (and also T_g). Inserting more network modifiers such as CaO and MgO into the glass structure leads to an increase in non-bridging oxygens bonds within the network. Hence, the glass with the lowest concentration of the network formers Al_2O_3 and SiO_2 (glass 7) has the lowest BO/T and thus the lowest network connectivity. This explains the decrease in T_3 as well: the lower the network connectivity, the smaller is the rigidity, i.e. the resistance to movement of the clusters in the melt and in consequence the lower is the viscosity. Therefore, the temperature at the viscosity of

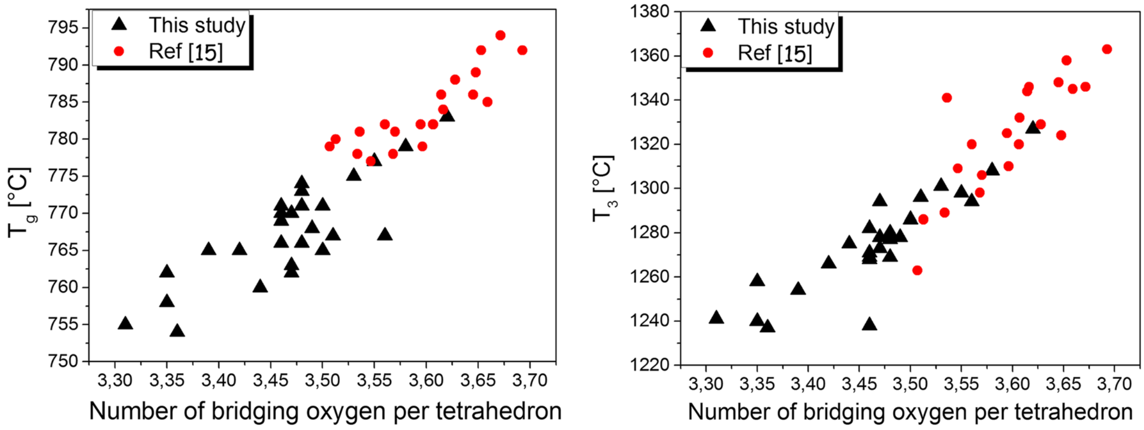

Figure 3 T_3 and T_g as a function of the number of bridging oxygen per tetrahedron.

10^3 dPa s, which is of interest in this study, is lower for glasses with high concentration of alkaline earths.

This is proved by the comparison of the 5 glass duos 15 and 27, 17 and 22, 2 and 14, 4 and 14, and 6 and 13, with almost identical Al_2O_3 and CaO concentrations: T_3 is significantly decreasing if SiO_2 is substituted by MgO.

Furthermore, if comparing glasses 4 and 12 with almost identical MgO and Al_2O_3 concentrations, it is visible, that the substitution of SiO_2 by CaO results in decreasing temperatures at a viscosity of 10^3 dPa s, just as expected. Other examples which show similar behaviour are the glass duos 16 & 8 and 11 & 13. Additionally, T_3 values from Ref. [16] without any MgO were compared to similar glass compositions from this glass series. In Table 3 and Fig. 4, the results are displayed and show a linear trend. If 5 mol% of SiO_2 are exchanged by MgO, T_3 decreases by 60–80 K. A substitution of 3.2 mol% MgO by SiO_2—hence, more network modifiers are in the system—increases T_3 by 66 K.

However, when interpreting Fig. 1—the front view—and also Fig. 2d the influence of the MgO concentration on the T_3 does not show a clear trend: it does not seem to be affected by increasing MgO concentrations. This is because the temperature of the CMAS-glasses depends more strongly on the CaO- than on the MgO concentration. The glasses 7, 8, 16 and 22, which have similar MgO concentrations of around 2.5 mol% showed increasing T_3-temperatures which are all between 1238 and 1327 °C (see Fig. 1 Front view/Table 2). This can easily be correlated with the increase in the CaO concentration (see Fig. 1, top view), which increases from 23.5 to 27.9 mol%. The direct comparison of different glass sets with similar concentrations of silica and alumina (1 and 7 and 12) shows that the substitution of CaO by MgO increases T_3. This is not observed in the glass sets 12 & 23 and 5 & 25; however, the temperature shifts of only 6 and 9 K, respectively, are within the error of the method and therefore not significant.

For the set 1, 7 and 12, an interesting effect was noticed if one network modifier is exchanged by another. For the glass duo 7 and 1, with increasing MgO concentration from 2.5 to 3.2 mol%, the temperature increases by 31 K, whereas from glass 7–12, even though another 1.4 mol% are added, the temperature changes only by 4 K. Also for the glass set 12 and 23, where the MgO—concentration is increased from 4.0 to 4.6 mol%, the measured temperature change is only 6 K, and for glass set 25 and 5, where the MgO concentration is increased from 3.6 to 5.4 mol%, the temperature change is only 9 K. Although in both sets, the temperature change is contradicting to the trend, it can still be concluded that the effect of the alkaline earths gets less pronounced if their concentrations are higher. It has already been described by, e.g. Vogel that the viscosity changes are less significantly if more alkaline network modifiers are added. In the glass compositions studied in this paper, this effect is also observed, if there is already a network modifier incorporated into the network (CaO) and a second one is added (MgO).

It was expected that the incorporation of MgO as substitute of the larger CaO would have a decreasing

Table 3 Change in the temperature T_3 due to substitution of SiO_2 by MgO

	SiO_2 (mol%)	CaO (mol%)	Al_2O_3 (mol%)	MgO (mol%)	T_3 (°C)
Glass 15	61.8	24.4	8.6	5.2	1297
Glass 27	62.6	24.2	8.8	4.44	1286
Δ	−0.8	0.2	−0.1	0.8	11
Glass 22	64.6	23.6	9.8	2.1	1326
Glass 17	63.6	23.7	9.6	3.1	1310
Δ	1.0	−0.2	0.2	−1.0	16
Glass 14	63.0	24.7	9.2	3.1	1292
Glass 2	62.6	24.8	9.3	3.4	1301
Δ	0.4	−0.1	−0.04	−0.3	−9
Glass 4	61.6	24.5	9.2	4.7	1286
Glass 14	63.0	24.7	9.2	3.1	1292
Δ	−1.4	−0.2	0	1.58	−6
Glass 20	61.7	26.6	8.3	3.5	1269
Glass 21	60.2	26.7	8.3	4.8	1294
Δ	1.5	−0.1	0.0	−1.3	−25
Glass 17 [16]	66.4	23.9	9.8	0.00	1346
Glass 21	62.5	23.8	9.7	4.0	1294
Δ	3.86	0.1	0.1	4.0	52
Glass 17 [16]	66.4	23.9	9.8	0.0	1346
Glass 17	63.6	23.7	9.6	3.1	1310
Δ	2.8	0.2	0.2	−3.1	36
Glass 15 [16]	64.9	26.0	9.2	0.0	1325
Glass 23	60.9	25.9	9.2	4.0	1279
Δ	3.9	0.1	0.0	−4.0	46
Glass 2 [16]	65.0	26.7	8.1	0.3	1341
Glass 6	60.2	26.7	8.3	4.8	1253
Δ	4.8	0.0	−0.2	−4.5	88
Glass 14 [16]	65.8	25.0	9.3	0	1329
Glass 2	62.6	24.8	9.3	3.4	1301
Δ	3.2	0.2	0.0	−3.4	28
Glass 2 [16]	65.0	26.7	8.1	0.3	1341
Glass 13	61.7	26.6	8.3	3.5	1275
Δ	3.3	0.1	−0.2	−3.2	66
Glass 14 [16]	65.8	25.0	9.3	0	1329
Glass 5	60.2	24.9	9.6	5.4	1269
Δ	5.6	0.1	−0.31	−5.4	60
Glass 8 [16]	64.9	25.9	9.2	0.0	1310
Glass 28	61.4	25.8	8.7	4.1	1271
Δ	3.5	0.2	0.5	−4.1	39

stimulus on the viscosity. Instead, as mentioned before, the T_3 values increase, the more CaO is exchanged even though the number of bridging oxygen is identical for each set. This is due to the more covalent character of the Mg–O bonds in comparison with the more ionic Ca–O bonds.

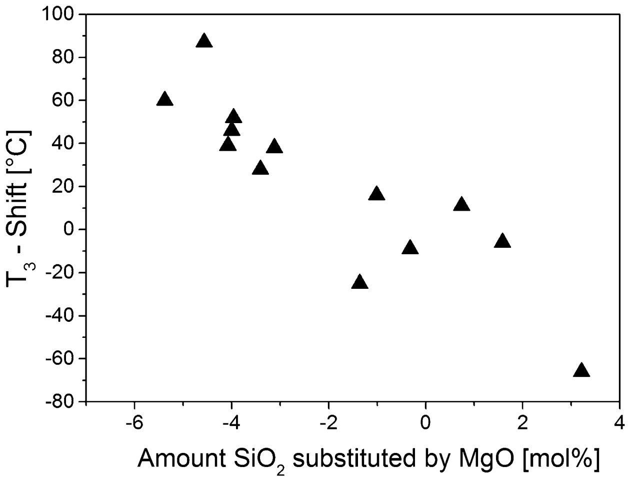

Figure 4 Shift of T_3 as function of the of substitution of SiO_2 by MgO.

The substitution of one network former atom against the other (Al_2O_3 vs SiO_2) does not have any impact on T_3: the glass sets 13 & 25 and 23 & 28, with similar CaO and MgO concentrations (as network modifiers) show both temperature shifts of only 3 and 9 K, which can be considered as identical within the error margin of the analysis. The substitution of 1 mol% SiO_2 against 1 mol% Al_2O_3 slightly increases the number of bridging oxygen within the network, because 2 aluminium tetrahedra are incorporated if only one silicon tetrahedron is taken out, but this obviously does not noticeably affect T_3.

Liquidus temperature T_{liq}

The liquidus temperatures determined via a tubular gradient furnace are listed in Table 2. With 20 tests of the same glass composition, the error distribution of the gradient furnace was determined to be 7 K. Liquidus temperatures of 1165, 1164 and 1169 °C were measured for the similar compositions 9, 19 and 26, respectively. In analogy, the glasses 3 and 28, also very comparable in composition, had values of 1138 and 1142 °C.

Within the investigated composition region, the temperatures vary between 1138 °C for glass 3 and a maximum value of 1192 °C for composition 7. All determined values were lower than expected in comparison with the liquidus temperatures given by the figures of Ref. [13], where only a temperature lower than 1300 °C was reported. Even though a liquidus temperature of 1130 °C for a composition next to the investigated composition range was reported by Koch et al. [15], higher values were expected because of the fact that not the eutectic but only a neighbouring range was examined.

The glasses with magnesium oxide concentration have a lower T_{Liq} range than the glasses from Ref. [16], which had liquidus temperatures varying between 1157 and 1214 °C.

ΔT: the difference between T_3 and T_{Liq}

Obviously, the composition changes of 6 mol% SiO_2, 4.3 mol% CaO, 2.0 mol% Al_2O_3, and 4.0 mol% MgO had a greater impact on the forming temperature at the viscosity of 10^3 dPa s than on the crystallisation of the glasses. In comparison with T_3, the T_{Liq}—data changed only by 53 K, whereas the temperature at a viscosity of 10^3 dPa s showed a difference of 90 K between the lowest and the highest measured values. Close to the eutectic range, liquidus temperatures usually drop significantly even with small composition changes. Hence, it was expected that T_{Liq} would show a more pronounced variation, whereas the viscosity and T_3 should not be influenced as strongly with those small variations in the compositions. From this observation, it can be concluded that the viscosity of the glasses is the decisive factor for ΔT.

In Fig. 5, the difference ΔT between the processing (T_3) and the liquidus temperature (T_{Liq}) as a function of composition is displayed. It is visible that the difference between the two temperatures T_3 and T_{Liq} varies between 65 and 160 K. Thus, all glasses would meet the requirement of $\Delta T = 50$ K and be suitable for the glass fibre-forming processes. To avoid the risk of interruptions due to crystallisations while forming the glass melt, a temperature difference of $\geq$70 K is more advantageous, which then excludes glass 18 (dark red) with a ΔT of 65 K.

But high values of ΔT, which guarantee process stability, are not the only parameter to consider. More energy is needed to produce the final product if the processing temperature of the glass melt is increased. Hence, a ΔT value, which is too high, is not favourable either. Nevertheless, all compositions with a ΔT higher than 70 K could probably be adjusted easily. With minor additions of alkali oxides such as lithium oxide, sodium oxide or potassium oxide, T_3 could be lowered without changing T_{liq} considerably [22]. However, glass compositions with a ΔT higher than 130 K should be excluded, because then T_3 is too high and the energy costs increase. Minor additions

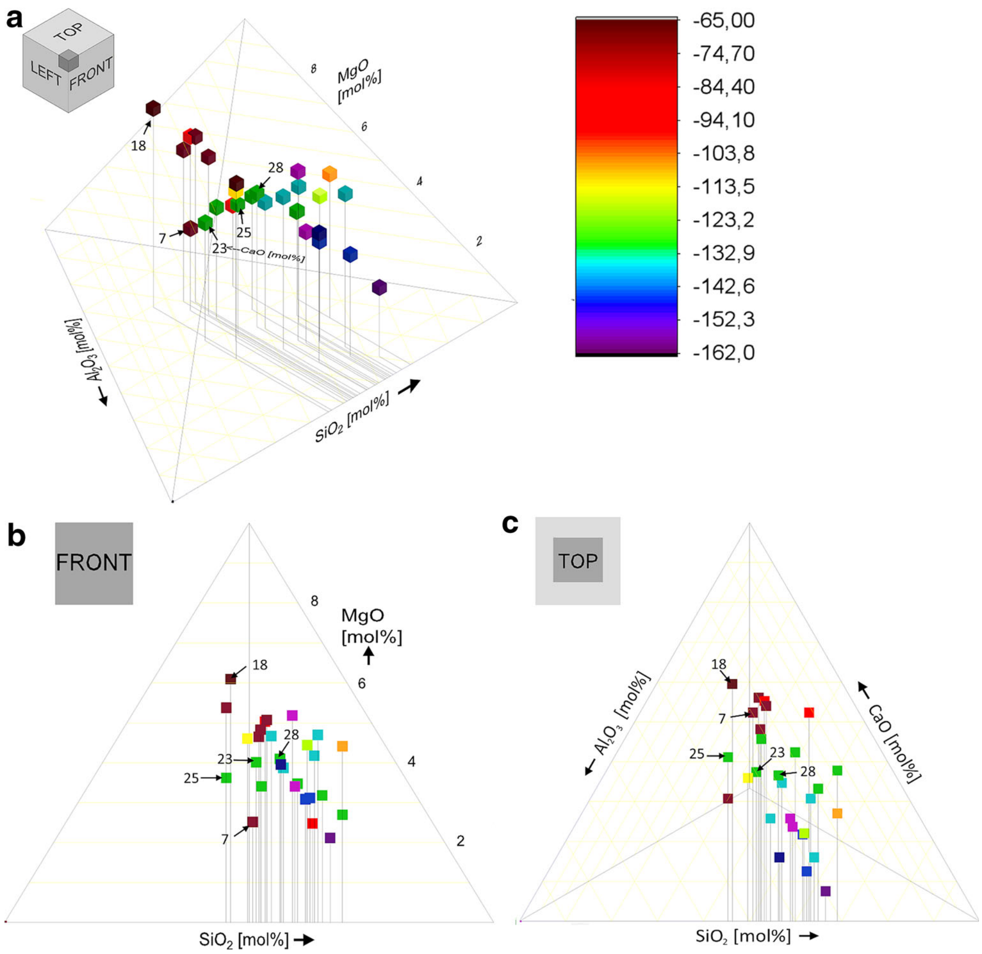

Figure 5 ΔT between T_3 and T_{Liq} as a function of the composition (mol%) in a 3D phase diagram, with view from *side* (**a**), *front* (**b**) and *top* (**c**).

of alkali oxides may not decrease T_3 sufficiently to get a suitable ΔT. For the glasses of this study, T_3 was the decisive factor for ΔT and is increased above 1300 °C, even though T_{Liq} is lower than 1160 °C. Hence, all glass composition with low calcium oxide composition would be a bad choice, because of their high working temperatures at a viscosity of 10^3 dPa s which leads to the favourable high ΔT but increase the energy costs ineffectively because the production requirements are already met with $\Delta T = 50$ K, which means they do not need to be significantly higher.

The more calcium oxide the compositions contain, the smaller is ΔT. This effect is achieved, because T_3 decreases to temperatures of around 1240 °C, whereas the liquidus temperature is increased to at least 1160 °C (glass 7) and up to 1192 °C (glass 18).

Small composition changes generally cannot be ruled out in the commercial glass production. This is why a composition range with the smallest risk to failure needs to be chosen. The best processing range for the glass melts should be within the green zone in Fig. 5 Top view, because firstly the liquidus temperatures do not change significantly (around 15 K) and are secondly also the lowest of the whole studied composition range. The working temperature is between 1270 and 1280 °C, leading to a ΔT of 110–120 K.

As mentioned above, the working temperature can be decreased with small additions of alkali oxides. Addition of 1 wt% Li_2O already decreased the working temperature of a glass with a similar composition by around 50 K [22].

In summary, even though the glasses 7 and 16 might have lower ΔT temperatures but the working temperature of the glasses 23, 25 and 28 can be adjusted to the same region as glasses 7 and 16. Hence, the energy needed to draw those fibres would be similar, but the difference to the crystallisation temperature would be higher because of the lower liquidus temperatures of the glasses 23, 25 and 28 and therefore more advantageous for a smooth production process.

Since the magnesium concentration within the glass compositions does not have any noticeable impact on ΔT (see front view in Fig. 5), it can be concluded, that for the choosing of the composition, the decisive factor is the calcium concentration, followed by the silica-concentration (top view in Fig. 5). The MgO concentration might therefore be the component to be changed easily—maybe in exchange for the alkali oxides. It is concluded that the composition of the glasses 23, 25 or 28 would be the most suitable choice as reinforcement glass fibre composition: they have sufficiently high ΔT and T_3 is comparatively small or can be adjusted.

Obviously, the production of commercial reinforcement glass fibres does not use laboratory raw materials but rather technical raw materials which contain tramp oxides, such as Fe_2O_3, TiO_2 or alkali oxides. It can be expected, that they also affect T_3 and T_{Liq} but it is not possible to predict reliable values for the influence of these tramps. Of course, the inclusion of network modifiers such as Fe_2O_3 or alkalies (which are also often tramps in technical raw materials) would definitely decrease T_3 for same the reasons explained earlier.

But the extent of the decrease cannot be predicted without exactly knowing in which raw material the tramps are included. If for instance the raw material clay is used for the glass melting which includes at least trace quantities of alkalies, the reduction of T_3 would be much higher, since the alkali oxides are then basically substituted for the network formers SiO_2 and Al_2O_3. But if the alkalies are coming into the melt through the raw material lime (which is a technical raw material for CaO) the effect is probably not as pronounced.

It is assumed that the crystallisation is inhibited the more components a glass melt contains, but it is not clear, whether the liquidus temperature is affected, or just the crystallisation rate. For all these reasons, it is not possible to estimate the variation of ΔT when technical raw materials are used instead of pure raw materials.

Conclusion

The design of new technologically important glasses requires a thorough knowledge on the effect of composition on key properties of the product. Altogether, 28 glasses with compositions between 23.9 and 28.6 mol% CaO, 2.7 and 5.0 mol% MgO, 7.6 and 9.6 mol% Al_2O_3, and 59 and 63.4 mol% SiO_2 were melted from pure raw materials. The composition of each glass sample was determined via X-ray fluorescence to ensure a correct comparison of the compositions and their influence on the thermal property values. The glass transition temperature, T_g, the forming temperature at a viscosity of 10^3 dPa s T_3 and the liquidus temperature T_{Liq} of the glasses were measured. T_g ranged from 754 to 783 ± 3 °C; T_3 varied between 1237 and 1327 ± 6 °C and T_{liq} between 1138 and 1192 °C ±7 K. It was found that the small composition changes had a larger effect on the viscosity than on the crystallisation temperature.

The network modifier calcium oxide had the major effect on viscosity changes, overlapping the influence of magnesium oxide. Substitution of SiO_2 by Al_2O_3 did not result in significant changes in viscosity. All glass compositions met the safety requirements of a minimum $\Delta T = 50$ K and are therefore suitable as reinforcement fibres although to ensure energy saving processes neither T_{Liq} nor ΔT should not be too high.

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