

Influence of alumina content and modifiers on phase separation in soda–lime–silica glass

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The phase separation behaviour of industrial soda–lime–silica glass is studied by visible light scattering. The main aspects which differentiate industrial glass from the ternary glass (composition in wt%): 76 SiO₂, 13 Na₂O, 11 CaO are considered. The obtained results show that the simple ternary glass easily develops phase separation upon annealing at suitable temperature levels. Conversely, container glass is stabilized against demixtion by the presence of a significant Al₂O₃ concentration, a significantly lower SiO₂ content and a more complex chemical formulation (partial substitution of SiO₂, Na₂O and CaO with Al₂O₃, K₂O and MgO, respectively, as well as minor ingredients).

Einfluß von Tonerdegehalt und Netzwerkwandlern auf die Phasentrennung in Kalk-Natronsilicatglas

Das Phasentrennungsverhalten von industriellen Kalk-Natronsilicatgläsern wird mit Hilfe der Lichtstreuung im sichtbaren Bereich untersucht. Die Hauptmerkmale, die das Verhalten der technischen Gläser von dem des ternären Glases (Massenanteil in %): 76 SiO₂, 13 Na₂O, 11 CaO unterscheiden, werden erörtert. Die Ergebnisse zeigen, daß das einfache ternäre Glas durch eine Wärmebehandlung bei entsprechenden Temperaturen zur Phasentrennung neigt. Behälterglas ist gegen eine Entmischung stabil bei einem signifikanten Al₂O₃-Gehalt, einem deutlich niedrigeren SiO₂-Gehalt oder einer komplexeren chemischen Zusammensetzung (teilweiser Ersatz von SiO₂, Na₂O, CaO durch Al₂O₃, K₂O, MgO sowie weitere geringe Beimengungen).

1. Introduction

Several papers [1 to 4] report phase separation for ternary soda–lime–silica compositions approximately similar to those of commercial glasses, i.e. with Na₂O, CaO and SiO₂ contents in the ranges 12 to 14, 10 to 12 and 75 to 76 wt%, respectively. Phase separation takes place by a nucleation and growth mechanism [5]. The tendency to produce demixtion decreases for lower SiO₂ contents, while the composition moves towards the immiscibility boundary. Within the composition range mentioned above the influence of even small oscillations of the modifier content was shown to critically affect the separation behaviour [1, 4 and 6]. Rindone et al. [3] and Kumar and Rindone [7] evidenced the influence of the water content in increasing the phase separation tendency for such ternary glasses. In addition, they pointed out the influence of alumina (for contents in excess of several hundred parts per million (ppm)) in drastically inhibiting phase separation.

Recently, the influence of the hydroxyl content on phase separation was confirmed by Jewell and Shelby [8]. McGinnis and Shelby [9], after an extensive review, concluded that the influence of water on phase separation varies with the glass composition. According to McGinnis and Shelby [10], water acts by lowering the vis-

cosity and therefore, by shifting the “nose” of the Time-Temperature-Transformation (TTT) curve (or the growth rate). Conversely, Al₂O₃ modifies both viscosity and surface tension and therefore also the immiscibility temperature.

The ternary system has been the object of extensive laboratory investigations. Nevertheless, there is a lack of systematic studies to predict accurately the behaviour of multicomponent industrial soda–lime–silica glass for containers and glazing. This glass is characterized by a significant substitution of silicon, sodium and calcium with aluminium, potassium and magnesium oxides, respectively, and by the presence of minor components such as Fe₂O₃, SO₃, BaO, PbO, TiO₂ and so on [11 and 12]. Studies of the influence of alumina impurities in ternary glasses were published by Rindone et al. [3] and Kumar and Rindone [7]. Other investigations by Topping and Murthy [13] and by Moriya [14] described the effects of alumina additions above 0.75 mol% to sodium silicate glasses. Nevertheless, no results are available about the influence of alumina above 1 wt% on demixtion in soda–lime–silica glass. Moreover, due to flame melting, the content of dissolved water (incorporated as hydroxyl or silanol, Si–OH groups) in industrial glass ranges between 300 and 400 ppm [12]. This corresponds to an amount at least twice the concentrations typically found in the above-mentioned (electrically melted) ternary

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glasses [7]. Accordingly, no reliable prediction can be made about the influence of Al_2O_3 , water and network modifiers other than sodium and calcium oxides content on phase separation. In principle, multicomponent glass can be treated as a pseudoternary system, adding the Al_2O_3 and Fe_2O_3 molar content to SiO_2 , K_2O to Na_2O and MgO to CaO . However, according to Benedetti et al. [11], predictions based on such simplified treatment fail when the influence of a variety of network formers and modifiers has to be taken into account.

In the past, several authors [15 to 18] attributed forming problems and strength losses affecting the production of container glass to phase separation, assuming a behaviour similar to the ternary glass (composition in wt%) 76 SiO_2 , 13 Na_2O , 11 CaO . However, no data about the behaviour of multicomponent industrial soda–lime–silica glass are found in the recent specialized literature. Very recently Albertini et al. [19] and Benedetti et al. [11] found no evidence of the presence of phase separation phenomena in a range of container and sheet glasses, the former by Small-Angle Neutron Scattering (SANS), the latter by Small-Angle X-ray Scattering (SAXS) and Visible Light Scattering (VLS).

The problem raised here is not only of scientific interest; in fact, a complete understanding of the presence of microstructure and of the conditions which lead to its formation would allow to control glass rheology and strength more properly [20 and 21].

The aims of this paper are:

- to perform a more systematic evaluation of the influence of alumina content on the tendency to develop phase separation in a ternary model glass with the same nominal composition as that studied by Rindone et al. [3] and in an industrial container glass;
- to verify the assumption of previous studies that the ternary soda–lime–silica glass with the composition (in wt%): 76 SiO_2 , 13 Na_2O , 11 CaO can realistically model the phase separation behaviour of industrial container glass. In order to monitor the phase separation process, VLS techniques are used.

2. Experimental procedure

2.1 Sample preparation

2.1.1 Model glasses (ternary laboratory-melted soda–lime–silica glasses with various alumina levels)

Analytical grade sodium and calcium carbonates and a high-purity silica sand (30 ppm Al_2O_3) were used as raw materials to produce a ternary glass with alumina at trace levels. 500 g of cord and seed-free glass were obtained by electrical melting at 1500 °C for 2 h and at 1400 °C for 14 h in a Pt/Rh 13% crucible. The melt was occasionally stirred to improve homogeneity. The melt was cooled in air and annealed at 550 °C. The glass was then extracted from the crucible by a diamond shell auger. The glass was divided in three parts. The first part was studied in the as-received condition; the second part was remelted at 1530 °C adding

0.1 mol% Al_2O_3 as $\text{Al}(\text{OH})_3$, the ratios among the other components being constant. The remaining glass was remelted at the same temperature adding 1 mol% Al_2O_3 , using the same procedures previously discussed.

Table 1 shows composition, water content and transformation temperature of the three glasses, which were labeled A, B, C, respectively. The water content was determined by infrared spectroscopy using the extinction coefficient of 40 l/(mol cm) at 2.8 μm as suggested by Geotti-Bianchini and De Riu [12]. The transformation temperature (T_g) was determined by Differential Thermal Analysis (DTA) using a heating rate of 20 K/min.

In order to check whether the phase separation behaviour of ternary glasses is critically influenced by the water content, small differences of composition and raw materials, three glasses nominally identical to glasses A, B and C, labeled as A', B' and C', were melted independently, using the same melting procedure previously described and a commercial Fontainebleau-type sand (300 ppm Al_2O_3) as a silica source.

Additionally, two other glasses labeled C'' and C''' with a composition nominally identical to C' but with different water content were melted using the same procedure. The water content was adjusted by bubbling the melt at 1400 °C with dry or water-saturated nitrogen. The analytical composition and water content of these glasses are reported in table 1.

2.1.2 Industrial soda–lime–silica multicomponent glasses

A clear soda–lime–silica glass for containers with 1.4 wt% Al_2O_3 was chosen as the glass with the highest alumina content (HA). The as-received material was remelted in an electric furnace at 1500 °C with occasional stirring in order to eliminate bubbles and inhomogeneous layers. The melt was held at 1400 °C for 14 h, cooled in air and annealed at 550 °C. Successively it was extracted from the Pt/Rh 13% crucible by means of a diamond shell auger. For comparison, a glass with the same composition but with alumina in trace amounts (TA) was melted, the molar ratios among the other components being kept constant. Raw materials for this second glass were high-purity silica (30 ppm Al_2O_3), reagent grade Na_2CO_3 , Na_2SO_4 , K_2CO_3 , CaCO_3 , Fe_2O_3 and technical MgCO_3 (containing 0.16% Al_2O_3). Glass TA was obtained with the same melting procedure as used for glass HA. The analytical composition, water content and transformation temperature of both glasses (together with the target composition of glass TA) are shown in table 1.

2.2 Heat treatments

Heat treatments were performed on at least three samples ((10 × 10 × 10) mm³), taken randomly from the lot.

The upper immiscibility temperature (T_m) is the temperature at which a given glass becomes clear again in a relatively short time due to redissolution of the phase separation formed at lower temperatures. In order to deter-

Table 1. Chemical composition (in wt%), water content and transformation temperature, T_g , for the glasses studied in this work. The theoretical (target) composition for glass TA is shown for comparison.

glass	A	B	C	A'	B'	C'	C''	C'''	HA	TA theoretical	TA experimental
SiO ₂	76.9	76.8	75.8	76.3	76.5	75.7	75.5	75.6	72.0	73.0	73.6
Al ₂ O ₃	0.003	0.12	0.93	0.04	0.13	0.76	0.94	1.06	1.4		0.01
Na ₂ O	12.6	12.6	12.5	13.0	13.0	12.9	12.6	12.7	13.2	13.4	13.4
CaO	10.3	10.4	10.6	10.5	10.3	10.5	10.8	10.4	9.2	9.3	9.2
MgO									2.9	3.0	2.7
K ₂ O									0.9	0.9	0.7
SO ₃									0.27	0.27	0.13
Fe ₂ O ₃									0.04	0.04	0.07
H ₂ O (in ppm)	120	230	215	130	120	150	120	305	213		105
T_g (in °C)	602	599	597						571		573

mine T_m the following approach was used. Initially, phase separation was promoted using suitable heat treatments, suggested by the literature of found by a trial-and-error procedure. Subsequently, each sample was annealed for 1 h at a temperature in the range of 660 to 780 °C (10 degrees steps), rapidly cooled and analyzed for VLS. The temperature T_m was reported as the lowest temperature at which a clear glass (producing no detectable light scattering) was obtained.

Heat treatments for at least 2 h above the upper immiscibility temperature allowed to produce samples reasonably free of phase separation nuclei. This condition is critical for accurately tracing TTT curves. These curves are obtained by plotting the annealing time at a given temperature necessary to produce the first detectable trace of opalescence. TTT curves were obtained by performing isothermal treatments for different times (ranging from 30 min to some tens of hours) at temperatures ranging between T_g and T_m and recording the shortest annealing time at which opalescence occurs.

Another important temperature to be determined, correlated to the well-assessed phase separation mechanism in this glassy system (i.e. by nucleation and growth), is the critical nucleation temperature T_{nc} ($< T_m$). This temperature defines the limit above which it is possible to observe growth, but not nucleation. In order to determine this temperature samples were heated above T_m and successively annealed for long times below T_m , decreasing the temperature by ten degrees steps, until phase separation could be detected.

2.3 Visible light scattering measurements

The collimated light beam of an optical microscope was used for a preliminary evaluation of the presence of phase separation, revealed by a pale blue opalescence due to Tyndall effect presence. For a semiquantitative evaluation, the intensity of light scattered at 90° by each sample was assessed by observing perpendicularly the brightness of the path of the beam of a 2 mW He-Ne laser crossing a polished glass block, as suggested by Scott and Rawson [22]. The unknown sample was compared with similarly

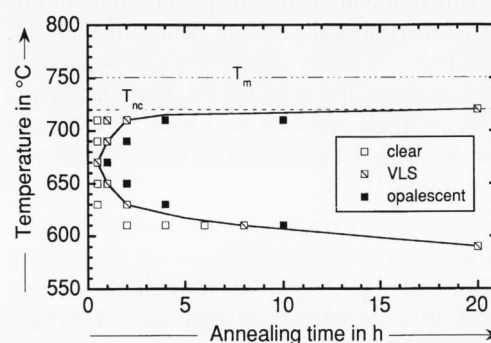


Figure 1. TTT curve for glass A showing the immiscibility temperature, T_m , and critical nucleation temperature, T_{nc} .

prepared blocks of a range of optical glasses, whose light scattering behaviour had been quantitatively assessed by Mörxbauer [23] and Steinert et al. [24]. Although the procedure is not quantitative, it is quite suitable to assess differences when different samples are compared. It was shown by Albertini et al. [19] and Benedetti et al. [11] that VLS provides results in good agreement with SANS and SAXS. These techniques detect inhomogeneities when the beam brightness is above a given threshold.

3. Results

3.1 Ternary model glass

3.1.1 Glasses A and B

For the determination of the upper immiscibility temperature T_m , previously discussed, suggestions by Rindone et al. [3] for glasses with similar composition were followed. A nucleation step at 615 °C for 1 h followed by a growth step at 650 °C for 2 h was used for this purpose. The marked phase separation thus obtained disappeared after annealing for 1 h at temperatures in excess of 750 °C.

Once T_m was determined, the critical nucleation temperature T_{nc} was found, following the procedure previously described. A complete TTT curve for the base glass (glass A) is shown in figure 1. It is possible to observe a small phase separation effect also for a temperature 10 K below T_g after an annealing treatment of 20 h.

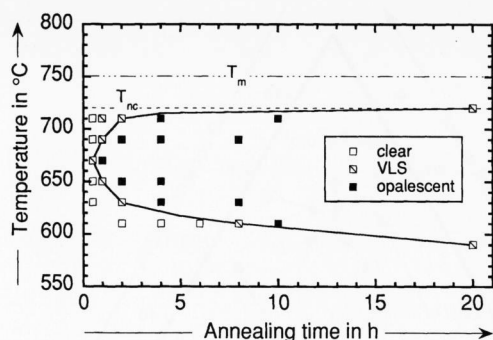


Figure 2. TTT curve for glass B showing the immiscibility temperature, T_m , and critical nucleation temperature, T_{nc} .

Table 2. Molar ratio for $\text{SiO}_2 (+\text{Al}_2\text{O}_3) : \text{Na}_2\text{O} : \text{CaO}$ and values of T_m and T_{nc} for glasses A and B and for similar compositions described in previous studies

	$\text{SiO}_2 : \text{Na}_2\text{O} : \text{CaO}$	T_m (in °C)	T_{nc} (in °C)
glasses A and B	76.7 : 12.2 : 11.0	750	720
Ohlberg and Hammel [1]	76 : 13 : 11	750	701
Yu-shen Xie and Brückner [6]	75 : 12.5 : 12.5	700	660
Huntebrinker et al. [4]	75.9 : 13.1 : 11	702	650

The TTT curve for glass B is shown in figure 2. The differences with respect to figure 1 are minor. Therefore, identical values of T_m and T_{nc} are reported in table 2.

3.1.2 Glasses A' and B'

In this case the only check performed was based on a range of heat treatments at 670 °C, corresponding to the "nose of the curve" (i.e., the temperature at which the TTT curves shown in figures 1 and 2 are closer to the y axis), followed by evaluation of the VLS level. For both A' and B' glass it was found that 1.5 h is sufficient to produce an appreciable increase of the light scattering level. After 3 to 4 h the Tyndall effect occurred.

3.1.3 Glasses C, C', C'' and C'''

Evidence of phase separation could not be obtained for any of these glasses, in spite of heat treatments prolonged up to 24 h in the temperature range between 600 and 700 °C. In the case of the corresponding alumina-free compositions this interval covers approximately the range between T_g and T_{nc} .

3.2 Industrial glasses

The temperature interval considered for glasses TA and HA ranged between 560 and 900 °C (i.e. between ≈ 10 K below T_g and ≈ 100 K below the liquidus temperature). Steps of 30 K and annealing times up to 90 h were used. In the case of thermal treatments above 700 °C, owing to surface crystallization, larger samples of both

glasses ($20 \times 15 \times 15$ mm³) had to be used in order to produce after polishing a glass volume sufficient for VLS observations. In this case the external crystallized layer was removed by grinding. No phase separation was observed in any sample of both glasses.

4. Discussion

4.1 Glasses A, B, A' and B'

As shown in table 2, T_m and T_{nc} values found for both A and B glass are in agreement with the values reported in previous studies for similar glass compositions [1, 2 and 6]. In order to compare different glasses, for compositions A and B the $\text{SiO}_2 : \text{Na}_2\text{O} : \text{CaO}$ molar ratio was computed by adding Al_2O_3 to SiO_2 (pseudoternary system). The differences in phase separation behaviour as compared to previous studies can be attributed both to compositional differences (including differences between nominal and actual composition) and to the effects of local compositional gradients due to imperfect melt homogenization [6]. When glass A is compared to glass B, no significant variation in phase separation behaviour is observed in association with the (moderate) introduction of Al_2O_3 (+ 0.1 wt%). According to Kumar and Rindone [7], even the small addition of Al_2O_3 associated with the use of impure commercial sand (+ 0.1%) was sufficient to totally suppress the development of phase separation in a glass with similar composition. This suggestion was not confirmed by the results obtained in this work for glasses B and B'. In spite of the small but significant variations of the ratios Si : Na : Ca : Al : OH (which might normally be expected to modify the phase separation behaviour), both glasses developed light scattering and Tyndall effect after annealing at 670 °C for 1.5 to 4 h.

4.2 Glasses C, C', C'' and C'''

Glasses C to C''' with an Si (+Al) : Na : Ca ratio similar to glasses A and B, alumina levels ranging between 750 and 1000 ppm and H_2O contents between 120 and 300 ppm showed no indication of phase separation. No inhomogeneity was detected even after a systematic set of prolonged heat treatments covering the temperature range between 600 and 700 °C which contains the "nose" of the TTT curve for the corresponding ternary glasses. This result shows that significant additions of Al_2O_3 (in the range of 1 wt%) to the soda–lime–silica glass system efficiently inhibit the tendency to undergo phase separation. This is in agreement with the results reported by Topping and Murthy [13] and Moriya [14] who added significant amounts of Al_2O_3 (0.75 to 1.5 mol%) to the $\text{Na}_2\text{O}-\text{SiO}_2$ system. It is interesting to remark that when the composition of glasses C, C'' and C''' is expressed in terms of a pseudoternary system, the ratio $\text{SiO}_2 (+\text{Al}_2\text{O}_3) : \text{Na}_2\text{O} : \text{CaO}$ remains substantially similar to those of glasses A, B, A' and B'. Therefore, as shown in figure 3, the corresponding points in the ternary diagram traced by Burnett and Douglas [2] fall well within the immiscibility boundary. This suggests that the substi-

tution of silicon with aluminium (for concentrations larger than a given threshold) is not indifferent for a correct prediction of the phase separation behaviour. According to Varshal [25] this can be explained by the difficulty to substitute the $[\text{SiO}_4]$ tetrahedra with sodium or calcium ion-stabilized $[\text{AlO}_4]$ tetrahedra.

4.3 Glasses HA and TA

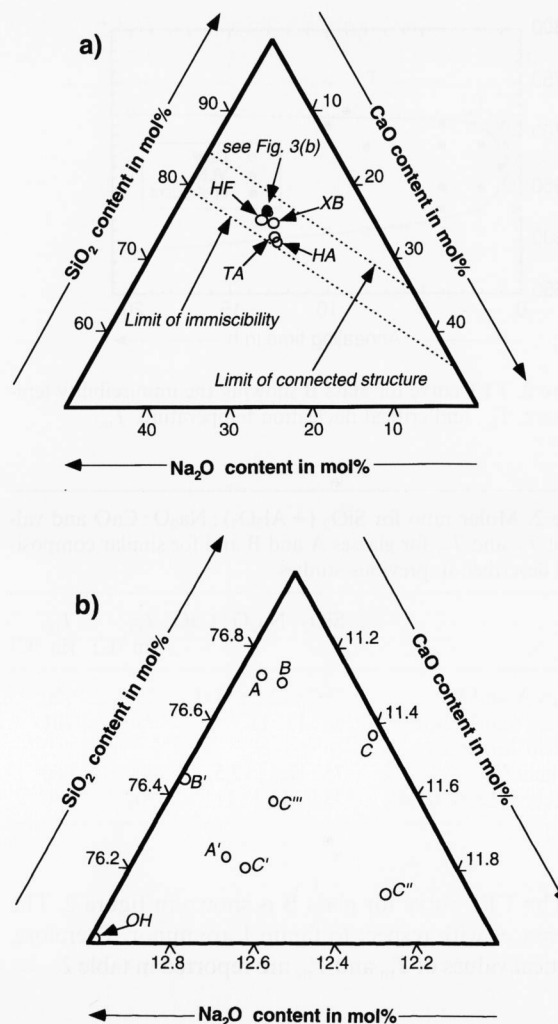
The commercial flint container glass (HA) and the laboratory-melted glass with approximately the same Si : Na : K : Ca : Mg ratio and the Al_2O_3 content decreased from 1.4 to 0.01 wt% (TA) did not show any phase separation effect. This behaviour was observed in spite of systematic attempts to achieve phase separation by prolonged heat treatment in a broad temperature range.

This result is in agreement with the results of Benedetti et al. [11] and Albertini et al. [19]. These authors were not able to induce any phase separation or any type of inhomogeneous features that could be detected using VLS, SANS or SAXS by annealing treatments performed according to several time-temperature programs on various types of commercial soda-lime-silica glass including container and flat glass. In agreement with the results of Benedetti et al. [11] and Albertini et al. [19], the present work suggests that there is a great difference in phase separation behaviour between commercial multicomponent glasses and ternary soda-lime-silica glasses with a composition similar to that of glass A.

As shown in figure 3, for glass TA, containing only 0.01 wt% Al_2O_3 , the ratio $\text{SiO}_2 : \text{Na}_2\text{O} (+ \text{K}_2\text{O}) : \text{CaO} (+ \text{MgO}) (\approx 72.4 : 13.2 : 14.2)$ corresponds to a point in the ternary diagram within the Burnett and Douglas [2] immiscibility boundary (though this point is significantly closer to it as compared to glasses A, B and C, due to its larger fraction of glass modifiers). This might predict for glass TA the possibility of phase separation. However, when the behaviour of glasses TA and HA is compared, the former shows no significant increase of the tendency to demixion. This result further confirms the hypothesis formulated by Benedetti et al. [11]: regardless the alumina content, the formulation of commercial glasses, with a variety of modifiers playing different structural roles, seems to be stabilized against demixion. In the work published by Goodman [26] the remark regarding the importance of alumina content in industrial glasses was formulated referring to the stability towards devitrification. According to the results obtained in this work, the argument can be extended also to phase separation.

5. Conclusions

The phase separation behaviour of glasses A and A' (soda-lime-silica glass with just traces of Al_2O_3) was in substantial agreement with literature suggestions. In the case of glasses B and B', where 0.1 wt% Al_2O_3 was introduced, the demixion behaviour did not change appreciably. In the case of glasses C, C', C'' and C''', where 0.7 to 1.1 wt% Al_2O_3 was introduced, the tendency to develop



Figures 3a and b. Position of the samples analyzed in the present work in the pseudoternary diagram for soda-lime-silica glass (adapted from Burnett and Douglas [2]). Glasses studied by Yu-shen Xie and Brückner (XB) [6], Ohlberg and Hammel (OH) [1] and Huntebrinker et al. (HF) [4] are shown for comparison; a) section corresponding to SiO_2 amount larger than 50 mol%, b) magnification of the portion containing the model glasses used in this work.

phase separation on annealing was totally suppressed. Such results show that while the presence of alumina impurities does not cause drastic effects per se, more significant additions in the order of 1 wt% efficiently inhibit demixion.

In the case of commercial multicomponent soda-lime-silica glass for containers, with significant substitutions of silicon with aluminium, of sodium with potassium and calcium with magnesium, no indication of phase separation could be detected. This result further confirms the stability of industrial soda-lime-silica glass against phase separation – previously documented by Albertini et al. [19] and by Benedetti et al. [11] – and shows that the phase separation behaviour of container and flat glass cannot be correctly predicted on the basis of the ternary system $\text{SiO}_2 : \text{Na}_2\text{O} : \text{CaO}$ with molar ratio $\approx 76 : 13 : 11$.

On the basis of the arguments just discussed, it is possible to point out that industrial multicomponent silica–soda–lime glass is stabilized against phase separation by the following factors:

- the ratio SiO_2 (+ Al_2O_3): Na_2O (+ K_2O): CaO (+ MgO) is shifted closer to the immiscibility boundary due to a substantial increase of network modifiers;
- a significant substitution of SiO_2 with Al_2O_3 , of Na_2O with K_2O and of CaO with MgO , together with the presence of a variety of minor ingredients (such as SO_3 , Fe_2O_3 and TiO_2) imparts the structure a complexity proportional to the number and variety of structural roles of the components;
- normally at least 1 wt% Al_2O_3 is present.

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