

Structural interpretation of the modification of soda-lime-silica glass properties by P_2O_5

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The influence of P_2O_5 addition on soda-lime-silica glass properties is discussed on the basis of a structural model. It involves two effects: insertion of phosphate molecular complexes into the silicate network interstices, and increase in silicate network condensation. The latter results from the scavenging of sodium and calcium cations by P_2O_5 . The properties considered in this paper are high-temperature viscosity and liquidus temperature. The P_2O_5 additions are in the 0.8 to 3.0 mol% range. The silica content of the glasses varies from 60 to 67 mol%, and the ratio $CaO/(CaO+Na_2O)$ from 0 to 0.85. Phosphate molecular complexes decrease the liquidus temperature and the high-temperature viscosity. Increasing the network condensation results in an increase in the viscosity, but its effect on the liquidus temperature depends on whether the glass composition lies on an upward or downward liquidus surface of the phase diagram.

Strukturelle Interpretation der Veränderung von Kalk-Natronsilicatglas-Eigenschaften durch P_2O_5

An Hand eines Strukturmodells wird der Einfluß der P_2O_5 -Zugabe auf Kalk-Natronsilicatglas-Eigenschaften diskutiert, die durch den Einbau des Phosphats als Molekülkomplex auf Zwischengitterplätze des Silicatnetzwerks und dessen Verdichtung hervorgerufen werden. Die Verdichtung des Silicatnetzwerks ergibt sich dabei aus der Bindung von Natrium- und Calciumkationen durch P_2O_5 . Untersucht wurden die Hochtemperaturviskosität und die Liquidustemperatur. Die Zugabe von P_2O_5 liegt im Bereich von 0,8 bis 3,0 Mol-%; der SiO_2 -Gehalt der Gläser variiert zwischen 60 und 67 Mol-% und das Verhältnis $CaO/(CaO+Na_2O)$ zwischen 0 und 0,85. Die Phosphat-Molekülkomplexe erniedrigen die Liquidustemperatur und die Hochtemperaturviskosität. Eine Zunahme der Netzwerkverdichtung führt zur Erhöhung der Viskosität; die Auswirkung auf die Liquidustemperatur hängt aber davon ab, ob die Glaszusammensetzung im Bereich der ansteigenden oder abfallenden Liquidusfläche des Phasendiagramms liegt.

1. Introduction

The effect of P_2O_5 on silicate glass properties is well documented because P_2O_5 is present in magmas as well as industrial glasses. This paper is related to the effect of small P_2O_5 additions (0.8 to 3.0 mol%) on the liquidus temperature and high-temperature viscosity of soda-lime-silica glasses. These two properties have to be considered in the elaboration process of industrial glasses:

Varshall et al. [1] reported that 0.3 wt% P_2O_5 , introduced as apatite ($Ca_{10}(PO_4)_6(OH)_2$), decrease the liquidus temperature of float glass by 20 to 30 K. 4 wt% P_2O_5 in $SiO_2-Al_2O_3-MgO-CaO-Na_2O$ glasses produce a 100 K decrease in the liquidus temperature, and decrease

the crystal growth rate [2]. Higher P_2O_5 quantity, e.g. 11 to 14 wt%, increases the liquidus temperature and leads to apatite as primary crystal [3]. The effect of P_2O_5 on the viscosity of $Na_2O-Al_2O_3-SiO_2$ glasses depends on the nature of the complexes that are formed [4]: the $AlPO_4$ complex increases the viscosity, whereas sodium phosphate complexes tend to decrease the melt viscosity. Dingwell et al. [5] reported that P_2O_5 decreases the viscosity of granitic melts of $K_2O-Na_2O-Al_2O_3-SiO_2$ compositions. In ferrobalt melts, P_2O_5 induces a reduction of Fe^{3+} into Fe^{2+} [6], hence less than 1 mol% P_2O_5 addition results in a decrease of the viscosity, whereas higher amounts produce an increase of the viscosity, owing to the network condensation.

Addition of P_2O_5 to a soda-lime-silica glass composition has two consequences [7]: the insertion of phosphate molecular complexes (namely monophosphates

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PO₄³⁻, and diphosphates P₂O₇⁴⁻) into the silicate network interstices, and increase in silicate network condensation. The latter results from the scavenging of sodium and calcium cations by P₂O₅. Although the effect of P₂O₅ on the silicate glass properties is often related to structural considerations, to our knowledge there is no study that distinguishes the specific effect of molecular phosphate addition from network condensation. We prepared soda-lime-silica glasses with compositions defined so as to separate these two potential effects.

2. Experimental procedure

The glasses were prepared in a Pt-10%Rh alloy crucible, heated by Joule effect between 1523 and 1823 K according to the glass composition. The raw materials were silica, sodium carbonate, calcium carbonate and sodium metaphosphate (NaPO₃). About 350 g batches were weighted, mechanically mixed, and melted at a temperature sufficient to obtain a melt viscosity lower than ca. 10 Pa s. The melt was homogenized by mechanical stirring with a platinum blade, then quenched on a steel plate, and annealed at T_g . All the glasses were analyzed by X-ray fluorescence.

The liquidus temperature was measured on 2 to 3 mm sieved glass powders. The samples are held in a platinum cone at a fixed temperature from 2 to 16 h in order to reach equilibrium. They are then polished and observed with a microscope for crystal detection. The liquidus temperature is defined as the highest temperature at which crystals are still observed.

The high temperature viscosity was measured between 1373 and 1823 K, with the rotating cylinder method. The crucible and cylinder were Pt-10%Rh alloy. The cylinder diameter is 16 mm and the height 32 mm. The rotation speed is adjusted between 0.05 and 780 min⁻¹, and the torque was measured with a Mettler RM260 rheometer. This equipment enables to measure viscosities in the range of 10⁵ to 10^{2.1} Pa s. All melt viscosities investigated in this study exhibit an Arrhenian behavior in the temperature range of the measurement.

3. Results

The glass compositions are reported in table 1. The silicate network condensation can be estimated from the average number of nonbridging oxygens per SiO₄ tetrahedron (NBO/T), calculated by the molar contents of the glass components:

$$\text{NBO/T} = 2(\text{Na}_2\text{O} + \text{CaO} - (3m + 2n)\text{P}_2\text{O}_5)/\text{SiO}_2,$$

where m and n are the molar proportions of mono- and diphosphate complexes, measured from ³¹P NMR spectra [7].

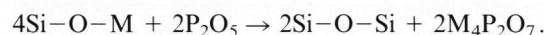
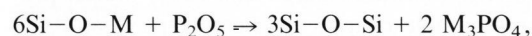
The labels A, B, C are defined in table 1. Starting from a reference glass A, we derived a glass C with higher silica content, i.e. with a higher network condensation. Glass B is then derived from glass C by addition of P₂O₅ with the charge-compensating Na⁺ and Ca²⁺ to form the mono- and diphosphate molecular complexes. Glasses B and C have then the same network condensation. The global effect of P₂O₅ addition on the considered properties can be observed by the comparison of glasses A and B. The glasses to which phosphate molecular complexes have been added (sodium and calcium salts of monophosphates PO₄³⁻, and diphosphates P₂O₇⁴⁻) are marked out in table 1 as reference glasses with (M^{x+}, PO₄^{z-}) phosphate complexes. The notation PO₄^{z-} represents both mono- and diphosphate molecules. Notice that the charge-compensating cations, designated as M^{x+}, are Na⁺ and Ca²⁺, in the same proportion as in the reference glass composition.

Table 2 shows the liquidus temperatures and the primary crystal phase present at the liquidus temperature. All the glasses containing phosphate molecular complexes have a lower liquidus temperature than the corresponding reference glass. The decrease in liquidus temperature is 20 to 40 K for glasses that contain 1.3 mol% P₂O₅. This effect on the liquidus temperature is observed for glasses with NBO/T equal to 1 or 1.33, whatever the CaO/(CaO+Na₂O) ratio is.

Figure 1 shows the evolution of the melt viscosities at 1523 and 1623 K, versus the amount of phosphates introduced in a 66.6SiO₂-33.4Na₂O glass. It can be seen that a glass to which phosphate molecular complexes have been added has a lower viscosity than its reference glass. This decrease is proportional to the amount of P₂O₅. Substitution of CaO for Na₂O in 66.6SiO₂-33.4Na₂O or 60.1SiO₂-39.9Na₂O glasses increases the melt viscosities (figure 2), as was already reported [8 and 9]. Phosphates introduced as mono- and diphosphate molecular complexes also decrease the melt viscosity, whatever the NBO/T or the CaO/(CaO+Na₂O) value. We noticed that the amplitude of the decrease in viscosity is constant within the measurement incertitude ($-0.13 \leq \Delta \lg \eta \leq -0.08$).

4. Discussion

Addition of P₂O₅ in a silicate glass leads to an increase in network condensation, and in the formation of mono- and diphosphate groups [10 to 13], according to the equations:



We have shown [7 and 13] that addition of 0.8 to 3 mol% P₂O₅ to Na₂O-SiO₂ or Na₂O-CaO-SiO₂ glasses, with a sufficient amount of Na₂O and CaO to maintain the local charge balance on monophosphate

Table 1. Analytical glass compositions (± 0.2 mol%), brief description of the glass composition, average number of non-bridging oxygen per tetrahedron (NBO/T, ± 0.02), glass labels, and CaO/(CaO+Na₂O) molar ratios (± 0.01)

no.	SiO ₂	CaO	Na ₂ O	P ₂ O ₅	description	label	NBO/T	CaO/(CaO+Na ₂ O)
1	60.1		39.9				1.33	0
2	66.6		34.4				1.03	0
3	63.2		35.7	1.1	glass 2+1.1 % (M ^{x+} , PO ₄ ^{z-})		1.03	0
4	61.8		36.5	1.6	glass 2+1.6 % (M ^{x+} , PO ₄ ^{z-})		1.03	0
5	58.1		38.9	3.0	glass 2+3.0 % (M ^{x+} , PO ₄ ^{z-})		1.03	0
6	59.9	13.0	27.1				1.34	0.32
7	57.0	13.6	28.2	1.2	glass 6+1.2 % (M ^{x+} , PO ₄ ^{z-})		1.34	0.32
8	60.2	19.9	19.9				1.32	0.5
9	57.0	20.9	20.9	1.2	glass 8+1.2 % (M ^{x+} , PO ₄ ^{z-})		1.34	0.5
10	60.1	26.8	13.1				1.33	0.67
11	57.0	28.1	13.7	1.2	glass 10+1.1 % (M ^{x+} , PO ₄ ^{z-})		1.34	0.67
12	60.2	33.6	6.2				1.32	0.85
13	57.4	35.1	6.3	1.2	glass 12+1.1 % (M ^{x+} , PO ₄ ^{z-})		1.32	0.85
14	64.0	17.9	18.1		glass 17 - SiO ₂	A	1.13	0.5
15	66.6	5.0	28.4				1.00	0.15
16	63.2	5.3	30.5	1.2	glass 15+1.1 % (M ^{x+} , PO ₄ ^{z-})		1.02	0.15
17	66.5	16.7	16.8		glass 14+SiO ₂	C	1.01	0.5
18	63.9	17.7	17.5	0.8	glass 17+0.8 % (M ^{x+} , PO ₄ ^{z-})	B	1.03	0.5
19	66.6	19.9	13.5				1.00	0.67
20	63.3	21.2	14.3	1.2	glass 19+1.2 % (M ^{x+} , PO ₄ ^{z-})		1.01	0.67
21	66.9	28.0	5.1				0.99	0.85
22	63.5	29.9	5.4	1.2	glass 4+1.2 % (M ^{x+} , PO ₄ ^{z-})		1.00	0.85

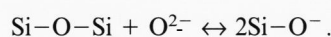
Table 2. Liquidus temperatures and primary crystal phases present at liquidus temperature

no.	SiO ₂	CaO	Na ₂ O	P ₂ O ₅	liquidus temperature in K	primary crystal phase at liquidus temperature
8	60.2	19.9	19.9		1454	n.d.
9	57.0	20.9	20.9	1.2	1434	n.d.
10	60.1	26.8	13.1		1537	α -CaSiO ₃
11	57.0	28.1	13.7	1.2	1503	α -CaSiO ₃
12	60.2	33.6	6.2		1653	α -CaSiO ₃
13	57.4	35.1	6.3	1.2	1633	α -CaSiO ₃
16	64.0	17.9	18.1		1382	Na ₂ O · 3CaO · 6SiO ₂
17	66.5	16.7	16.8		1352	β -CaSiO ₃
18	63.9	17.7	17.5	0.8	1335	β -CaSiO ₃
19	66.6	19.9	13.5		1448	α -CaSiO ₃
20	63.3	21.2	14.3	1.2	1408	α -CaSiO ₃
21	66.9	28.0	5.1		1613	α -CaSiO ₃
22	63.5	29.9	5.4	1.2	1573	α -CaSiO ₃

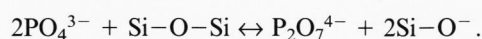
Note: - liquidus temperatures are given with an accuracy of ± 10 K;
 - n.d. stands for not detected.

groups (PO₄³⁻) and diphosphate groups (P₂O₇⁴⁻), does not modify the short range order of the silicate network. In particular, no silicate network condensation was observed with ²⁹Si nuclear magnetic resonance. Despite the low sensitivity of ²⁹Si NMR, the introduction of a small amount of P₂O₅ (without Na₂O and CaO) indeed produces a measurable change on the spectra [7 and 12]. Thus the phosphate groups can be considered as molecular complexes that are inserted into the silicate network interstices, without direct connection between the silicates and phosphates. Moreover, the relative amount of mono- and diphosphate groups is dependent upon the glass basicity [13]. A higher basicity induces a higher

amount of monophosphates, as a result of the acid base reactions that occur in the melt:



The balance is:



In soda-lime-silica glasses, the phosphate equilibrium is shifted toward the formation of monophosphate groups [7] as a consequence of calcium monophosphate complex formation.

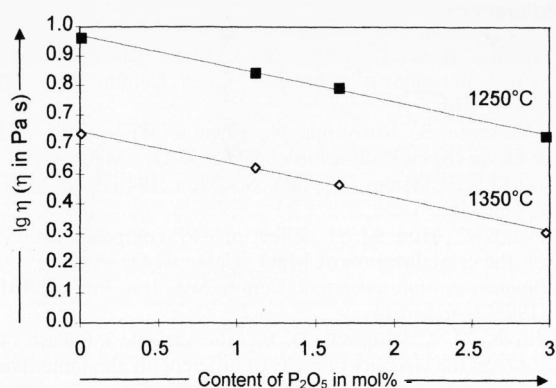


Figure 1. Viscosities of a 66.6SiO₂-33.4Na₂O glass at two temperatures versus the amount of P₂O₅ added as mono- and diphosphate molecular complexes. Error bars are within the size of the symbols.

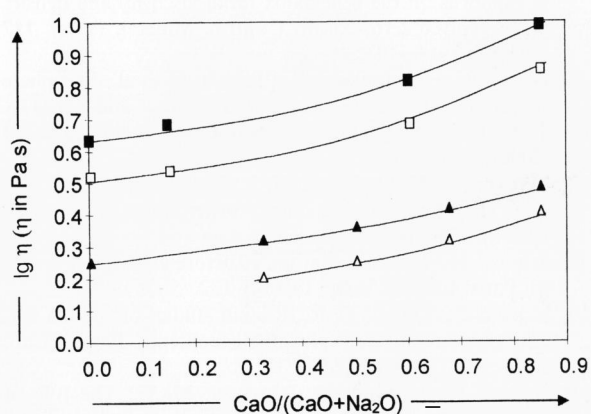


Figure 2. Viscosity of 66.6SiO₂ · (33.4 - x)Na₂O · xCaO glasses (squares) and 60.1SiO₂ · (39.9 - x)Na₂O · xCaO glasses (triangles) at 1623 K. The open symbols are the glasses containing 1.3 mol% P₂O₅ added as sodium and calcium mono- and diphosphate molecular complexes. Error bars are within the size of the symbols.

So, there are two structural parameters that have to be considered for the interpretation of the role of P₂O₅ on properties: the introduction of mono- and diphosphates as molecular complexes, and the network condensation.

Table 1 shows that the addition of P₂O₅ as molecular complexes, without changing the network condensation, results in a systematic decrease in the liquidus temperature. This is related to the Raoult and Clausius-Clapeyron laws. These laws express the liquidus depression caused by the addition of a second component to a melt [14]. Hence a decrease in the liquidus temperature should be observed as phosphate molecular complexes are added, i.e. as the glass composition moves from glass C to glass B. The effect of the network condensation on the liquidus temperature can be seen on the Na₂O-CaO-SiO₂ equilibrium phase diagram. Glass C is indeed derived from glass A by silica addition, so the composition moves toward the silica corner on the phase diagram. Since the glass C and

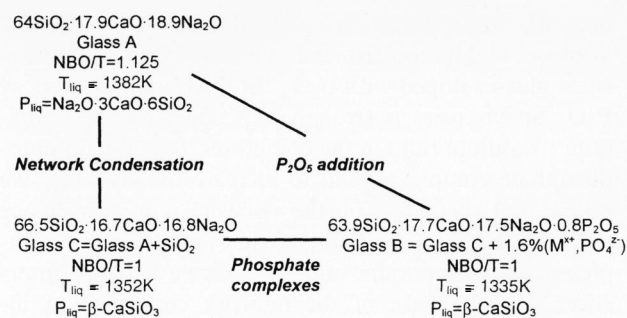


Figure 3. Effect of P₂O₅ addition on the liquidus temperature of a soda-lime-silica glass. P_{liq} are the crystals present at the liquidus temperature.

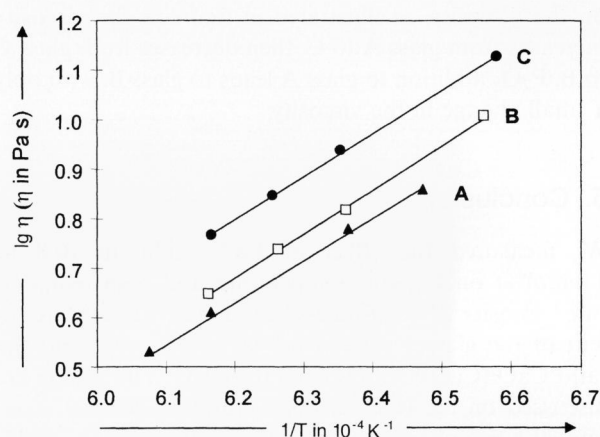


Figure 4. Effect of P₂O₅ addition on the high temperature viscosity of a soda-lime-silica glass. See figure 3 for the signification of labels A,B,C. The linear curve are fits corresponding to the Arrhenius law. Error bars are within the size of the symbols.

A compositions are located on downward (to SiO₂) liquidus surfaces of Na₂O · 3CaO · 6SiO₂ and β-CaSiO₃, the liquidus temperature will decrease with silica addition. Indeed, glass A (64SiO₂-17.9CaO-18.1Na₂O) has a liquidus at 1382 K, and glass C (66.5SiO₂-16.7CaO-1.8Na₂O) has a lower liquidus at 1352 K. Notice that the silica content should be higher than 72 mol% to move to the upward cristobalite liquidus surface. Finally the decrease of the liquidus temperature of 64SiO₂-17.9CaO-18.1Na₂O glass after P₂O₅ addition is due to two effects, that are resumed in figure 3: the decrease due to the network condensation, and a further decrease produced by the addition of the phosphate molecular entities.

Small addition of phosphates as molecular complexes, without changing the silicate network condensation, decreases the melt viscosity. This effect has been observed on every glass, independent of the amount of P₂O₅ (figure 1), CaO/Na₂O ratio (figure 2), and NBO/T value (figure 3). At high temperature, enthalpic effects, that reflect the average bonding strength, govern the viscous flow [15]. Hence the addition of phosphate complexes, with a lower bonding strength than the silicate

network one, induces the observed decrease in viscosity. Toplis et al. [4] reported similar effects in soda-alumino-silica glasses doped with P_2O_5 . In this case, the effect of P_2O_5 on viscosity is strongly dependent on the aluminum to sodium ratio in the complexes, because aluminophosphate complexes tend to increase the viscosity. We notice that this effect on the viscosity is in accordance with the structural assumption that the phosphate complexes are incorporated into the silicate network interstices. The increase of the network condensation increases the high-temperature viscosity [8 and 9]. Hence the effect of P_2O_5 addition on the viscosity is the result of two opposite effects: a decrease due to the insertion of phosphate complexes, and an increase due to the network condensation. Finally, P_2O_5 has only a small effect on the viscosity, as illustrated in figure 4: the viscosity increases from glass A to C, then decreases from glass C to B. P_2O_5 addition to glass A leads to glass B, with only a small change in the viscosity.

5. Conclusion

We measured the effect of P_2O_5 additions (0.8 to 3.0 mol%) on liquidus temperature and high temperature viscosity of soda-lime-silica glasses. The silica content of the glasses varies from 60 to 67 mol%, and the ratio $CaO/(CaO+Na_2O)$ from 0 to 0.85. The results are discussed on the basis of a structural model that separates the two effects due to P_2O_5 additions in the soda-lime-silica glasses: insertion of mono- and diphosphate complexes into the silicate network interstices, and increase of the silicate network condensation. Addition of phosphate complexes in soda-lime-silica glasses decreases the viscosity and the liquidus temperature, whatever the silica content, the $CaO/(CaO+Na_2O)$ ratio, and the amount of P_2O_5 are. In the composition range investigated in this study, network condensation increases the high-temperature viscosity, and decreases the liquidus temperature. But its effect on the liquidus temperature actually depends on the location of the glass composition on the equilibrium phase diagram. P_2O_5 addition on the considered properties is the resulting effect: it has little effect on the glass viscosity, and decreases the liquidus temperature in the composition range investigated in this paper.

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