LIQUIDUS TEMPERATURE AND STRUCTURE OF THE GLASS MELTS IN THE 15 Na_2O.10 (MgO, CaO, TiO_2, ZrO_2) . 75 SiO_2 SYSTEM

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The liquidus temperature in the 15 Na_2O.10 (MgO, CaO, TiO_2, ZrO_2).75 SiO_2 glass system was measured. The data have been used for the indication of the structural role of TiO_2 in this glass system. From the values of liquidus temperature the activity of SiO_2 in the melt was calculated according to Le Chatelier-Schreder equation. The analysis of liquidus temperature, based on the SiO_2 activity coefficient evaluation indicates, that Ti^{4+} forms discrete anionic complexes with modifying cations.

INTRODUCTION

The knowledge of the dependance of the liquidus temperature on composition is the basic prerequisite for the glass technology optimization and development of new glass compositions, respectively. Therefore, the quantity of the experimental data of the liquidus temperature concerning various glass forming systems has been published during past decades [1-4]. Though such obtained data have been determined for glass technology, in many cases there are possibilities to use them in interpretation of structural role of individual oxides in the glass melts.

The one of such interpretations of the liquidus temperatures was shown by Ryerson [5]. His work was based on the fact, that structural rearrangements produced by mixing additional components with SiO_2 are reflected in the variations of equilibrium silica activity $a(SiO_2)$ and activity coefficient $\gamma(SiO_2)$. These values may be considered as temperature independent if the values of mixing enthalpies are neglected. Variations in the activity coefficient of SiO_2 due to the changes in metal oxide type and concentration depend upon the manner in which these oxide components interact with the SiO_2 network.

The solution of alkali and alkaline earth oxides in SiO_2 causes the depolymerization of silicate network, which results in the formation of nonbridging oxygen bond complexes. The depolymerization mechanism produces positive deviations from ideality increasing with cation field strength. In Figure 1 there are plotted changes of activity coefficient of silica for cristobalite saturated melts in M_xO_y-SiO_2 systems at 1550 °C as a function of mole fraction of metal oxide component added [5]. It is evident, that the activity coefficient of SiO_2 increases systematically as the field strength of the alkali metal and alkaline earth metal cations increases.

The solution of the oxides with highly charged cations as Al^{3+}, Ti^{4+}, P^{5+} does not form nonbridging oxygen bond complexes. In this situation the cations Al^{3+}, Ti^{4+}, P^{5+} substitute Si^{4+} in the silicate network. This substitution produces negligible small positive and negative deviations from ideality in the binary systems (Figure 1).

In Figure 2 there are plotted changes of activity coefficient $\gamma(SiO_2)$ versus $x(MO) / [x(MO) + x(MgO)]$ in cristobalite-clinoenstatite saturated liquids at 1550 °C [5]. Substitutions of K_2O, Na_2O and CaO for MgO produce decreases in $\gamma(SiO_2)$; this is consistent with their effect relative to MgO in the binary systems.

The data for binary and ternary systems suggest that the role of network-modifying components in deviating the activity coefficient of SiO_2 will be qualitatively similar in both the compositionally simple and more complex liquids.

Also the effect of Al^{3+} in the deviating of $\gamma(SiO_2)$ is qualitatively similar in both types of liquids. Substitution of $PO_{2.5}$ and TiO_2 for MgO increases the activity coefficient of SiO_2 relative to that in the MgO-SiO_2 system. The relative effect of $PO_{2.5}$ and TiO_2 in the ternary system is reversed from that in the binaries. This suggests a change in their structural role. This change is consistent with a change in solution mechanism from that of network forming components to that of discrete anion forming components. The forming of discrete phosphate and titanium metal oxide bond complexes are reflected in the strong positive deviations from ideality.

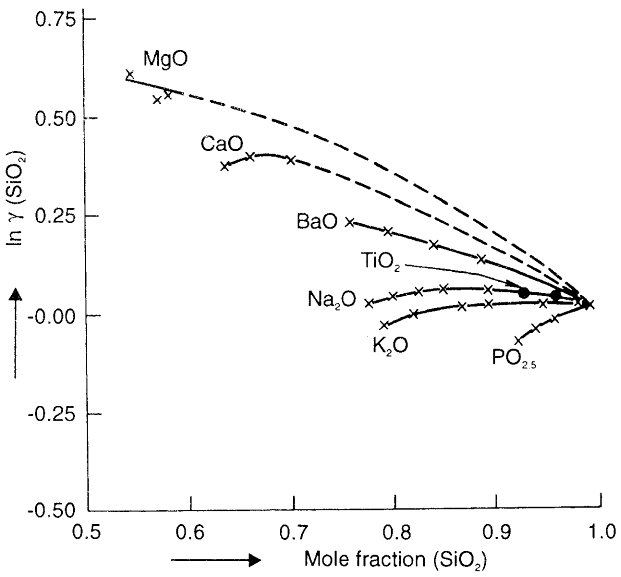

Figure 1. Logarithm of the activity coefficient of SiO_2, $\gamma(SiO_2)$, in cristobalite-tridymite saturated binary liquids versus the mole fraction of SiO_2 in the liquid (data from Ryerson [5])

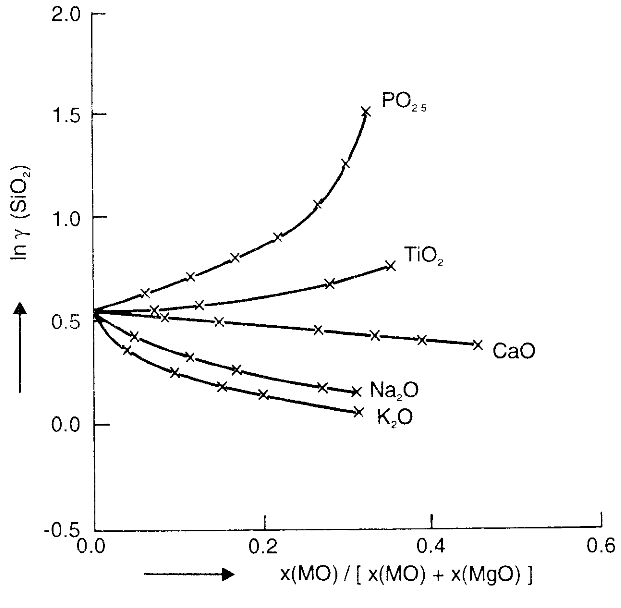

Figure 2. Logarithm of the activity coefficient of SiO_2, $\gamma(SiO_2)$, in cristobalite-clinoenstatite saturated liquids versus $x(MO)/[x(MO)+x(MgO)]$ in the liquid (data from Ryerson [5])

The main aim of the present work is to deduce the structural role of TiO_2 from the values of liquidus temperatures of studied glasses.

EXPERIMENTAL

Batches were prepared from glass sand, zirconium silicate and chemically pure TiO_2, Na_2CO_3, $MgCO_3$ and $CaCO_3$ and melted in a furnace at temperatures between 1500 and 1550 °C in a Pt-10%Rh crucible. Homogeneity was ensured by repeated fritting and hand-mixing of the glass during melting. Each melt was poured from the crucible onto a stainless steel plate. The samples were tempered in a muffle furnace for one hour at 600 °C, after which the furnace was switched off and samples allowed to remain there until completely cool.

The chemical composition of individual samples was determined by ICP emission spectral analysis after the samples had been decomposed by melting with lithium tetraborate.

The liquidus temperature t_{liq} was determined by keeping a sample of coarsely ground glass in a Pt-30%Rh boat in a gradient furnace for 24 h; the temperature at which the first crystal appeared in the sample was the liquidus temperature. The crystalline phases were determined by transmitting microscope.

RESULTS AND DISCUSSION

In this work the authors present the structural interpretation of liquidus temperature in the $15\,Na_2O.10\,(MgO,CaO,TiO_2,ZrO_2).75\,SiO_2$ glass system. The measured values have been used as input data in optimalisation of the glass composition suitable for production of alkaliresistant glass fibres [6,7].

The range of compositions investigated was delineated by a configurational tetrahedron with apices C, T, Z and M corresponding to melts with the following compositions, mol%:

C: $10CaO$, $0TiO_2$, $0ZrO_2$, $0MgO$, $15Na_2O$, $75SiO_2$
T: $0CaO$, $10TiO_2$, $0ZrO_2$, $0MgO$, $15Na_2O$, $75SiO_2$
Z: $0CaO$, $0TiO_2$, $10ZrO_2$, $0MgO$, $15Na_2O$, $75SiO_2$
M: $0CaO$, $0TiO_2$, $0ZrO_2$, $10MgO$, $15Na_2O$, $75SiO_2$

On the four triangle faces the figurative points of samples were distributed regularly according to the simplex scheme [8] as shown in Figure 3. This scheme gives 34 distinct melt compositions to which the Q composition located in the tetrahedron center was added

Q: $2.5CaO$, $2.5TiO_2$, $2.5ZrO_2$, $2.5MgO$, $15Na_2O$, $75SiO_2$

The chemical compositions of the glasses together with identified liquidus temperatures and primarily crystallized phases are listed in Table I.

The SiO_2 (cristobalite and/or tridymite) was primarily crystallized in the 24 glass compositions. The schematic of the glass compositions with SiO_2 as primarily crystallized phase is in Figure 4. In Figure 4 it can be seen that from the apices of glass compositions C, T, Z and M the SiO_2 crystallized only in the M and T apices. The wollastonite crystallized in the apex C and in the line connection C-T (beside apex T). The primarily crystallized phase have not been identified in the apex Z and in its glass composition vicinity. In this sample due to high value of viscosity crystal did not grow to the visible magnitude for 24 hours. In our previous work [1] we have identified zircon in the glass composition similar to glass composition Z. We suppose that in the region of glass composition of apex Z the zircon will crystallize as a primarily phase. In the remaining glass samples where primarily crystallized phase was not determined, probably crystals with low crystallization speed were present.

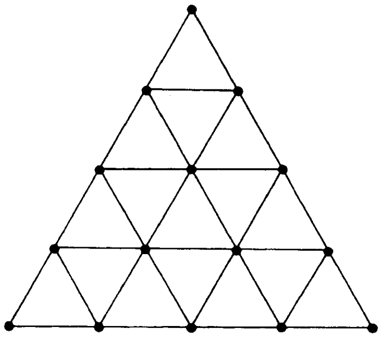

Figure 3. Schematic of the placing of the glass samples investigated

Table I. Chemical compositions of the glass samples (mol%), liquidus temperature t_{liq} and primarily crystallized phase (wo - wollastonite, tr - tridymite, cr - crystobalite).

	Na_2O	CaO	MgO	ZrO_2	TiO_2 x (%)	SiO_2	t_{liq} (°C)	phase
1	14.6	10.48	0.0	0.0	0.0	74.92	1167	wo
2	14.55	0.0	0.0	0.0	9.26	76.19	1282	tr
3	15.35	0.0	0.0	9.78	0.0	74.87	870	--
4	14.43	0.0	9.57	0.0	0.0	75.99	1172	tr,cr
5	14.69	5.23	0.0	0.0	4.9	75.18	1228	wo
6	15.13	5.2	0.0	5.09	0.0	74.58	1092	tr
7	14.71	4.85	4.99	0.0	0.0	75.45	1172	--
8	14.92	0.0	0.0	4.59	4.82	75.67	1075	tr
9	14.54	0.0	5.4	0.0	6.06	74.0	1203	tr,cr
10	14.72	0.0	5.27	5.02	0.0	74.99	991	cr
11	14.83	2.42	0.0	0.0	7.18	75.57	1247	wo
12	15.09	2.32	0.0	7.38	0.0	75.22	789	--
13	14.79	2.62	7.58	0.0	0.0	75.01	995	tr,cr
14	14.74	0.0	0.0	7.73	2.39	75.14	831	--
15	15.01	0.0	7.94	2.55	0.0	74.5	1000	cr
16	14.95	7.45	0.0	0.0	2.5	75.1	1126	wo
17	14.93	6.93	0.0	2.5	0.0	75.64	1056	cr
18	14.31	7.54	2.66	0.0	0.0	75.49	1131	--
19	14.52	0.0	0.0	2.52	7.22	75.74	1074	tr
20	14.76	0.0	2.74	0.0	7.99	74.5	1219	tr,cr
21	15.02	0.0	2.73	7.61	0.0	74.65	1077	--
22	14.68	4.64	0.0	2.01	2.25	76.43	1083	cr
23	14.73	4.92	2.43	2.49	0.0	75.44	1090	cr
24	15.04	2.34	0.0	2.13	4.7	75.79	1064	tr
25	14.61	2.55	0.0	4.61	2.15	75.54	1049	cr
26	15.12	2.47	2.65	5.0	0.0	74.75	948	tr,cr
27	14.95	2.28	4.54	2.47	0.0	75.76	1212	cr
28	14.71	0.0	2.32	2.38	5.16	75.43	1072	cr
29	14.57	0.0	2.37	5.11	2.39	75.57	800	--
30	14.79	0.0	4.58	2.5	2.39	75.75	882	cr
31	14.57	2.54	2.30	2.51	2.4	75.68	1019	cr
32	14.34	0.32	8.08	0.0	2.52	74.74	1175	tr,cr
33	14.26	5.36	2.54	0.0	2.48	75.36	1192	tr,cr
34	14.8	2.71	2.71	0.0	5.25	74.53	1175	cr
35	14.45	2.77	5.33	0.0	2.54	74.91	1142	tr,cr

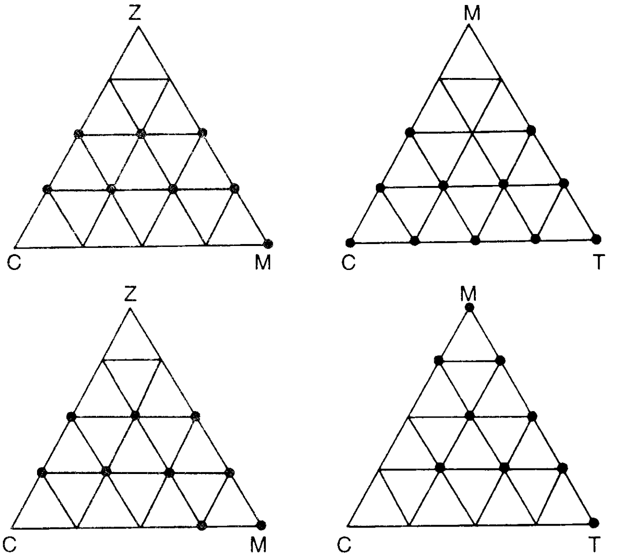

Figure 4. The schematic of the glass compositions with SiO_2 as primarily crystallized phase in the glass samples investigated.

From the values of liquidus temperature the activity of SiO_2 in the melt was calculated according to Le Chatelier-Schreder Equation (1):

$$\ln a(SiO2) = (\Delta H_f / R)\,(1 / T_f - 1 / T_{liq}) \qquad (1)$$

where $a(SiO2)$ is the activity SiO_2 in the melt, T_f is the melting temperature of the cristobalite, ΔH_f is the molar enthalpy of fusion of pure SiO_2 at T_{liq}. The temperature dependance of ΔH_f was neglected. The value of $\Delta H_f = 9.6$ kJ mol^{-1} at T_f 1996 K was taken in this calculation.

The activity coefficient $\gamma(SiO_2)$ was expressed by Equation (2):

$$\gamma(SiO_2) = a(SiO_2) \,/\, x(SiO_2) \qquad (2)$$

where $x(SiO_2)$ is the mole fraction of SiO_2 in the glass.

The sample in the apex M has the glass composition $15Na_2O.10MgO.75SiO_2$. In the line connecting M-T compositions the content MgO is regularly substituted by TiO_2 up to apex T with the composition $15Na_2O.10TiO_2.75SiO_2$. The change of activity coefficient $\gamma(SiO_2)$ in this line connection is possible to qualitatively compare with the results of Ryerson [5], where he investigated the change of activity coefficient SiO_2 caused by substitution TiO_2 for MgO in the $MgSiO_3$-SiO_2 system.

In the Figure 5 there is plotted the dependance of $\ln \gamma(SiO_2)$ versus ratio $x(TiO_2) / [x(TiO_2)+x(MgO)]$ in a line connection of glass compositions M-T. As it can be seen from Figure 5, the glass in the apex M (without TiO_2 content) has a small positive deviation from ideality. It is in agreement with the results of Ryerson [5] (Figure 1), where composition $25Na_2O.75SiO_2$ has a small negative value of $\ln a(SiO_2)$. The substitution 10 % of Na_2O by 10 % MgO (apex M) produces increase of activity SiO_2 to a small positive value. By substitution TiO_2 for MgO in the line connection M-T glass compositions the $a(SiO_2)$ increases with increasing TiO_2 content. The increase of this substitution is not such apparent as in the $MgSiO_3$-SiO_2 system due to buffering influence of Na_2O present in the glasses investigated.

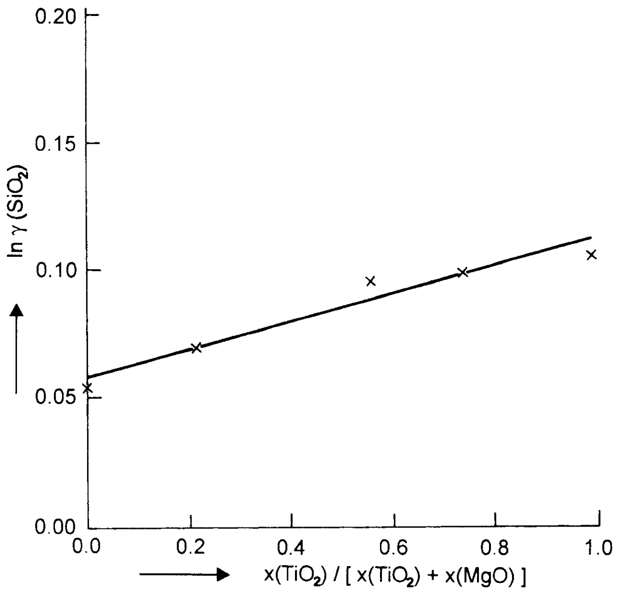

Figure 5. Logarithm of the activity coefficient of SiO_2, $\gamma(SiO_2)$, versus ratio $x(TiO_2)/[x(TiO_2) + x(MgO)]$ in the line connection of glass composition M - T

CONCLUSION

Applicating the results of Ryerson [5] we can conclude that Ti^{4+} forms discrete anionic complexes with modifying cations in the compositional range of studied glasses.

Acknowledgement

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TEPLOTA LIKVIDUS A ŠTRUKTÚRA V SKLOTVORNOM SYSTÉME $15Na_2O.10(MgO, CaO, TiO_2, ZrO_2).75SiO_2$

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Na základe nameraných hodnôt teploty likvidus v sklotvornom systéme $15Na_2O.10(MgO, CaO, TiO_2, ZrO_2).75SiO_2$ sa interpretovala štruktúrna úloha TiO_2 v sledovanej oblasti zložení skiel. Analýza hodnôt teploty likvidus vychádzala zo skutočnosti, že štruktúrne zmeny v tavenine zapríčinené prídavkom zložiek miešajucich sa s SiO_2 sa odrážajú v zmene aktivity $a(SiO_2)$ a aktivitného koeficienta $\gamma(SiO_2)$.

Z hodnôt teploty likvidus v zloženiach skiel, u ktorých bola identifikovaná ako primárne kryštalujúca fáza SiO_2, bola podľa Le Chatelier-Šrederovej rovnice vypočítaná aktivita $a(SiO_2)$ a následne aktivitný koeficient $\gamma(SiO_2)$.

Interpretácia štruktúrnej úlohy TiO_2 v sledovanom systéme bola založená na výsledkoch práce Ryersona [5], ktorý sledoval zmenu aktivitného koeficienta SiO_2, $\gamma(SiO_2)$, zapríčinenú náhradou TiO_2 za MgO v systéme $MgSiO_3$ - SiO_2.

Aplikujúc výsledky práce Ryersona [5] je možné na základe výsledkov dedukovať, že Ti^{4+} vytvára v sledovanom sklotvornom systéme aniónové komplexy s modifikujúcimi katiónami, v dôsledku čoho náhradou TiO_2 za MgO aktivitný koeficient vzrastá.