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Structures of Sodium Silicate Glass

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ABSTRACT

The structural model of sodium silicate glass plays a crucial role in understanding the properties and the nature of binary glass and other more complicated silicate glasses. This work proposes a structural model for sodium silicate glass based on the medium-range ordering structure of silica glass and the information found from the Na_2O-SiO_2 phase diagram. This new model is different from previous ones. First, the sodium silica glass is both structurally and chemically heterogeneous on the nanometer scale. Secondly, the sodium cation distribution is Na_2O concentration-dependent. In order to reflect the structural change with Na_2O concentration, it requires two different schematic graphs to present the glass structure. The model can be extended to other binary and multiple component silicate glasses and can be experimentally verified.

1. Introduction

In 1938, B. E. Warren published his classical work regarding the sodium silicate glass structure following several papers on silica glass structure [1]. Warren studied five different sodium silicate glass samples and concluded that Na atoms cause non-bridging oxygens in the glass network. The positively charged Na ions are thought to be incorporated "interstitially" in the vicinity of negatively charged non-bridging oxygens. These sodium ions and the associated non-bridging oxygens are randomly distributed in the system. The structure is statistically homogeneous. Figure 1 is the well-known two-dimensional schematic graph for a sodium silicate glass proposed by Warren [1]. The random network formed by SiO_4 tetrahedra in these sodium silicate glasses is consistent with Zachariasen's continuous random network (CRN) model [2].

However, the above random network structural model for sodium silicate glass has been challenged over the years. Attempts have been made to derive more precise structural information, such as interatomic distance and bond angle distribution in the silicate glasses. Experimentally measured average separation distance of atoms in the silicate glasses have contradicted the random network model [3]. In the 1980s, N. Greaves applied extended X-ray-absorption fine-structure spectroscopy (EXAFS) technique to study the very local structures of elements in the glasses [4,5]. The method detects each

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element's X-ray absorption edge and probes the individual pair distribution functions for the material separately. This method is particularly advantageous for studying the weakly bound cation like Na in multi-component oxide glasses. To match the experimental results, Greaves proposed the modified random network (MRN) model shown in Figure 2 [4]. The figure shows that the local environments of modifiers like Na_2O in glasses are incorporated in a complementary way with the network formers like SiO_2. The overall structure will necessarily comprise two-interlacing sublattices: the network regions constructed from network formers and the inter-network regions made up of modifiers, such as Na atoms. The MRN model is characterized by percolation paths or channels for modifying components. It explains many of the physical and diffusion-related properties of oxide glasses and can be viewed as an improved random network model [6].

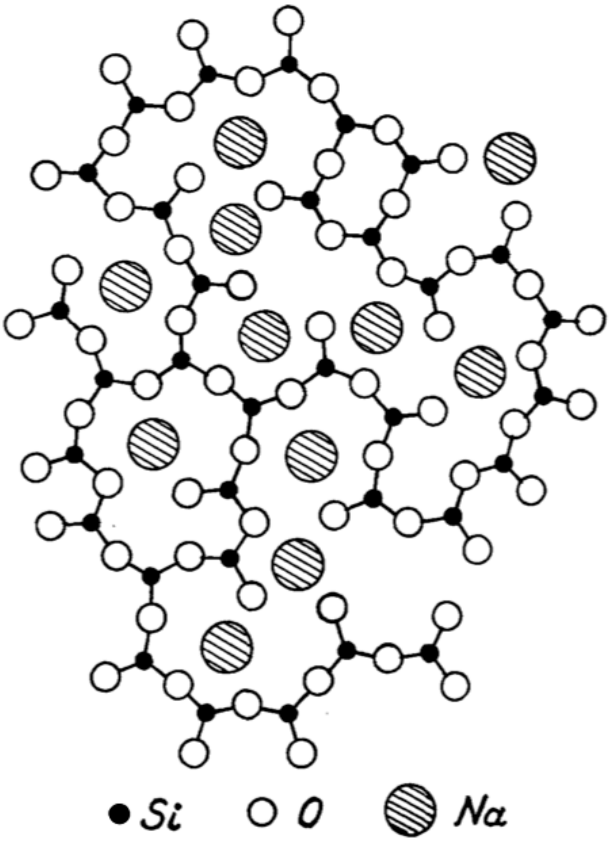


Figure 1. The well-known two-dimensional schematic diagram of CRN theory for a sodium silicate glass. (Reproduced from Ref. 1)

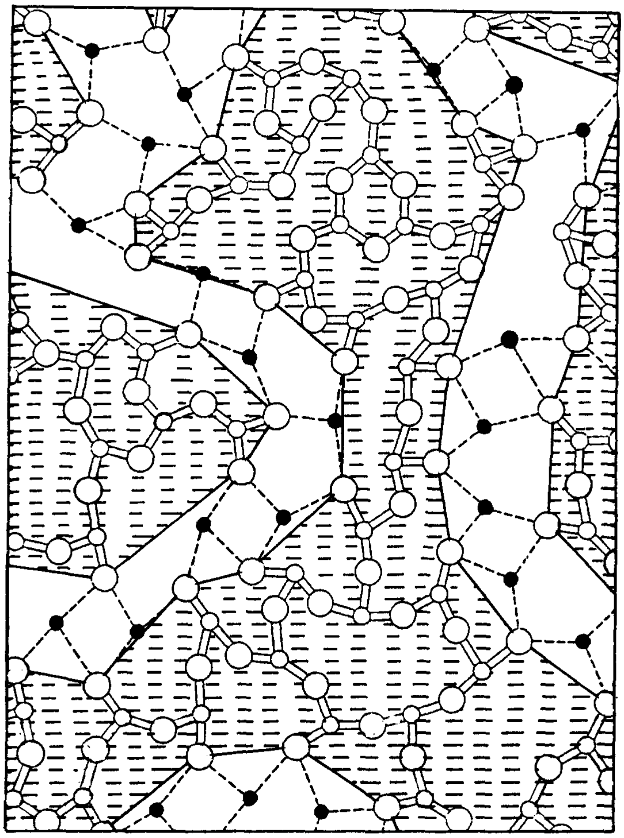


Figure 2. Modified random network model of sodium silicate glass and other alkali silicate glass. (Reproduced from Ref. 4)

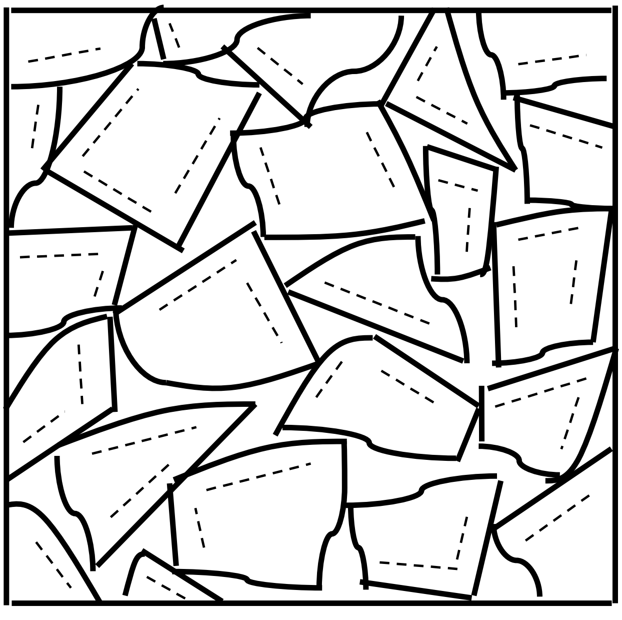
Although the MRN model incorporates the specific local structure of modifying cations and non-bridging oxygens within a CRN framework, the model does not reflect the medium-range ordering structure that may exist in the structure. Moreover, the MRN model does not reflect the changes of the medium-range structure as the concentration of added modifier increases. Therefore, there is a need to improve the MRN model further. The purpose of this work is to present a new structure model, which reflects the medium-range ordering and its variations with changes of Na_2O concentration in the sodium silicate glass.

2. Sodium Silicate Glass Structure Based on the Nanoflake Model

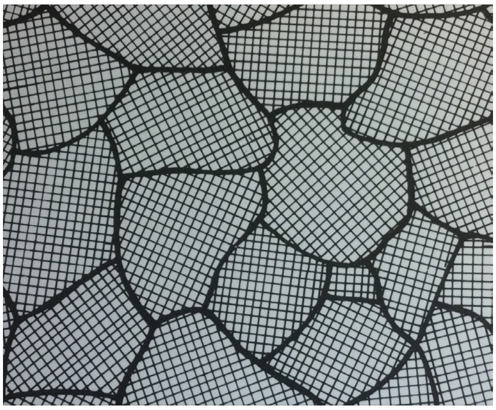
The nanoflake model describes the medium-range ordering structure in silica as 'nanoflakes' [7,8]. The flakes are formed by two layers of SiO_4 tetrahedra with a thickness of about 0.8 nm and lateral extension of about 2 nm. Adjacent nanoflakes intersect each other forming a cluster with a shape that is approximately octahedral. The clusters are randomly orientated and distributed in the system such that bulk isotropy is preserved. Figure

3(a) is the two-dimension schematic representation of the silica glass structure based on the nanoflake model. The figure shows that silica glass is structurally heterogeneous in the medium range. The dashed lines inside the clusters represent one-dimensional ordering structure on the facets of the clusters. The spaces between the clusters are occupied by more disordered structures. Figure 3(b) is a typical two-dimension polycrystal picture [9]. Compared to Figure 3(b), Figure 3(a) has the following significant characters:

(1) The size of the clusters in Figure 3(a) is only 1 or 2 nm, which is a few orders more diminutive than the size of the regular grains in Figure 3(b). (2) The clusters are not crystals and have only one-dimension ordering structures on the facets. In contrast, all grains in Figure 3(b) are crystals with 3-dimension ordering structures. (3) In Figure 3(b), all grains are contacted with the adjacent grains through grain boundaries. The boundaries are various and depend on the orientations of the adjacent grains. The thickness of the boundaries is usually less than the length of unit cell of the crystal. In contrast, the space between the clusters of Figure 3(a), is filled with chains, rings, or sheets formed by SiO_4 tetrahedra. A large portion of oxygen atoms located on the facets of the clusters do not bond with outside structures [8]. But those oxygen atoms located on the edges of the clusters can connect with outside structures.



a



b

Figure 3. (a) The two-dimension schematic graph of the silica glass structure. The dashed lines inside clusters represent one-dimensional ordering structure on the facets of the clusters. (b) The two-dimension graph of the normal polycrystals. All grains are three-dimensional ordering structure with various orientations. The interfaces of the grains are the grain boundaries. (Reproduced from Ref. 9)

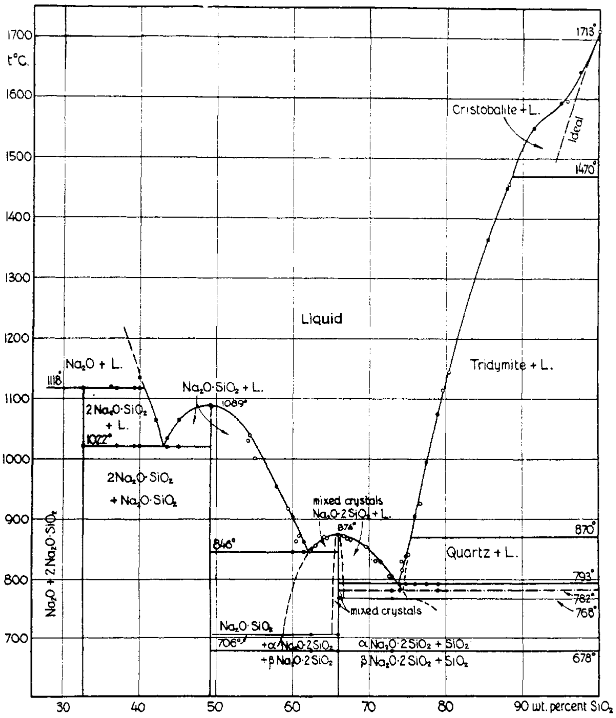


Figure 4. The Na_2O-SiO_2 phase diagram.

The figure shows that in the Na_2O concentration range from 0 to 25.5 weight%, the melting temperature of the binary glass decreases as the concentration of sodium oxide increases. The corresponding crystal form for sodium silicate glasses with sodium oxide in the range from 25.5 to 34 weight% is $Na_2Si_2O_5$. (Reproduced from Ref. 10)

For polycrystals shown in Figure 3(b), the grain boundaries are the preferential site for the segregation of impurities, forming a thin layer with different compositions from the bulk. One may think that the sodium oxide or other oxides added to silica glass will aggregate in the space between the clusters shown in Figure 3(a). However, the actual situation might be more complicated. Figure 4 is the Na_2O-SiO_2 phase diagram [10], which indicates that the liquidus temperature of the binary glass decreases as the concentration of sodium oxide increases. For sodium silicate glasses with more than 11.3% sodium oxide, the liquidus temperature is lower than 1470°C, which is the critical temperature of pure silica glass [8,11]. All clusters in silica glass are initially formed above the critical temperature as the embryo clusters of β-cristobalite and then transformed to the stabilized clusters in the lower temperature range [8]. From Figure 4, the β-cristobalite embryos can only be formed in the temperature region higher than 1470°C. Therefore, due to the low liquidus temperature of the sodium silicate glasses with more than 11.3 weight% of sodium oxide, the cluster structures may be different from that shown in Figure 3(a). Because there are four different temperature ranges of cluster formation from 0 up to 34 weight% of sodium oxide, the structures of sodium silicate glasses may be analyzed according to the four different composition ranges:

(1) Na_2O in the range of 0 - 11.3 weight%

From Figure 4, the liquidus temperature of sodium silicate glass decreases from 1713°C to 1470°C as sodium oxide increases to 11.3 weight%, and the β-cristobalite is the formed crystal in this temperature range. This indicates that the entire process of β-cristobalite crystal formation, including the embryo formation does not involve with the sodium cations. If the supercooled liquid is cooled fast enough, at the critical temperature of 1470°C, the crystal nuclei have not been formed. Then the embryonic clusters of β-cristobalite start to form nanoflakes on the facets, and the sodium cations can't bond with the oxygen atoms located inside of the clusters. Thus, the added sodium cations with the associated no-bridging oxygens would not appear inside the clusters in Figure 3(a). Therefore, the added sodium atoms in the sodium silicate glass distribute in the spaces between the clusters, as schematically shown in Figure 5(a).

(2) Na_2O in the range of 11.3 – 24.5 weight%

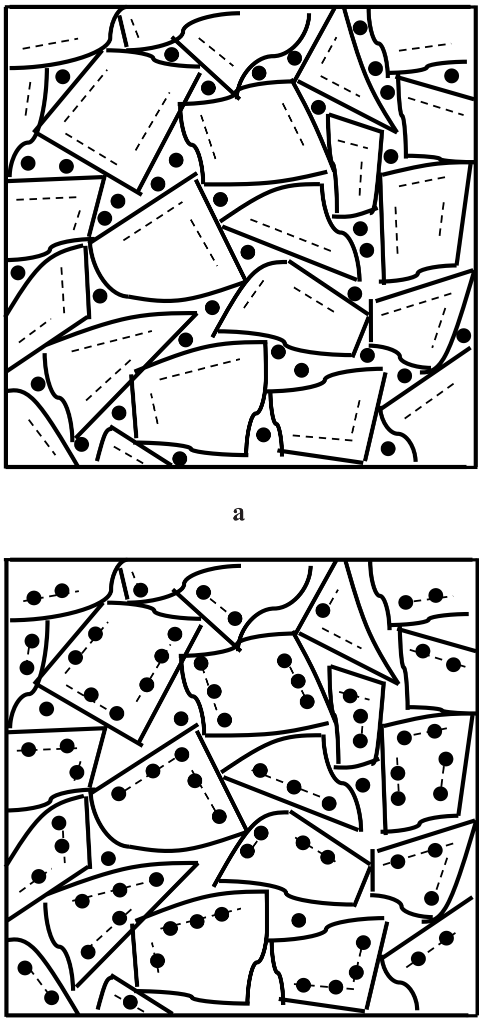
From Figure 4, the liquidus temperature of sodium silicate glasses in this composition range decreases from 1470°C to 870°C. The corresponding crystal form in this temperature range through which the sodium silicate glass solidifies is the β-tridymite, not the β-cristobalite. In the course of slow cooling, the β-tridymite crystals will be formed. Similarly, as in the temperature range higher than 1470°C, the sodium cations are not involved in the formation of embryonic clusters of β-tridymite. In the glass transition process, the sodium cations can't bond with the oxygen located inside of clusters. Thus, the structure of glass in this composition range may correspondingly be described by Figure 5(a) schematically. Noting the hexagonal structure of β-tridymite, the embryonic cluster of β-tridymite may have a different shape and number of facets than that of β-cristobalite.

(3) Na_2O in the range of 24.5 – 25.5 weight%

From Figure 4, the liquidus temperature of sodium silicate glasses in this composition range decreases from 870°C to 793°C. The corresponding crystal form in this narrow temperature range through which the sodium silicate glass solidifies is quartz. Similar to that discussed in the above two paragraphs, the glass structure in this composition range may also be schematically described by Figure 5(a), as long as the clusters in Figure 5(a) represent the transformed embryonic clusters of quartz nuclei.

(4) Na_2O in the range of 25.5 – 34 weight%

Figure 4 shows that as the weight% of Na_2O increases from 25.5 to 34, glass liquidus temperature does not decrease but increases from 793°C to 874°C. The different liquidus temperature behavior suggests that in this composition range, the Na_2O plays a different role in the sodium silicate glass structure. The corresponding crystal form in temperature range from 793°C to 874°C is not pure silica but $Na_2Si_2O_5$ crystal. In the crystallization process, the sodium cations participate in the formation of the clusters. Thus, not all the sodium cations can stay in the space between the clusters, and Figure 5(a) cannot represent structures of glasses in this composition range. Instead, Figure 5(b) may describe them schematically. In Figure 5(b), most sodium cations are inside the clusters with an one-dimension order structure on the facets. A small portion of sodium cations is still left in the spaces between clusters. The exact distribution of sodium is cooling rate dependent.



a

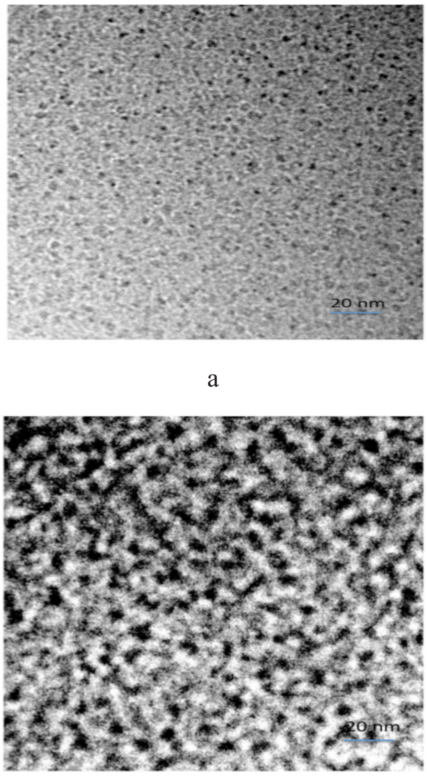
b

Figure 5. The schematic pictures of the sodium silicate glasses. The solid circle represents the Na cation. (a) Na_2O in the range of 0 – 25.5 weight%. (b) Na_2O in the range of 25.5 – 34 weight%.

3. Discussions

The proposed model shown in section 2 indicates that sodium silicate glasses are structurally and chemically heterogeneous in the nanoscale. There are two kinds of structures interconnected with each other inside glasses. One kind of structure is clusters transformed from embryos of crystal nuclei with an one-dimension ordering on the facets. Another kind of structure is distributed in the spaces between the clusters and is less ordered and may form short chains or sheets. All clusters are connected with others directly on the edges or indirectly through structures between them. In the composition range with less than 25.5 weight% Na_2O, the sodium cations are distributed in spaces between clusters, as shown in Figure 5(a). In this Na_2O composition range, the proposed model is very similar to the MRN model, except for the one-dimension ordering structure on the clusters' facets. Both models predict that the sodium cations in the glass segregate disorderly and eventually become continuous channels once their concentration reaches the percolation threshold. The percolation path formation inside glasses has been detected by various analytical techniques [6].

Sodium segregation and channels inside the sodium silicate glasses may be directly observed by TEM. A substantial amount of TEM papers studying the phase separation in glasses have been published [12-15]. However, most of these works use replica techniques for specimen preparation, and the spatial resolution is limited to about 10 nm. For the current study, better spatial resolution is necessary. The recently developed Fresnel contrast technique (a phase contract technique) can be applied for the TEM observation [16,17]. Figures 6(a) and 6(b) reveal the droplet-phase with 3nm in diameter in the matrix and the interpenetrated phase separation with a cross-section of 6 nm in two kinds of Pyrex glasses, respectively. Both Figs. 6(a) and 6(b) demonstrate the TEM method's ability for nanometer phase separation investigation. The details of this technique can be found in references [16,17].



a

b

Figure 6. Nano-phase separation in the Pyrex glasses revealed by TEM Fresnel contrast images. (a) droplet-phase with 3nm in diameter in the matrix. (b) the interpenetrated

phase separation with cross-section of 6 nm.

The proposed model differs noticeably from the MRN model in that it predicts existence of Na cations inside the clusters for sodium silicate glasses with NaO_2 concentration higher than 25.5 weight%. Because of the one-dimensional ordering on the facets of clusters, the average distance between Na cations should be very close to that in the $Na_2Si_2O_5$ crystal. Therefore, the proposed model further predicts that in this concentration range the Na cations' average distance would hardly change with its concentration variations. This prediction is consistent with the previously published EXAFS experimental results [5].

The model can also be straightforwardly extended to other binary silicate and more complicated silicate glasses, as long as the phase diagrams of the corresponding compounds are available. For example, Figure 7 is the SiO_2-CaO phase diagram [18]. The figure shows that as the CaO concentration increases to about 36 weight%, the liquidus temperature decreases to 1436°C. However, further increase in the CaO concentration causes the liquidus temperature to rise, and the corresponding crystal is not silica polymorph but $CaSiO_3$. The facts learned from the phase diagram (Figure 7) indicate that Ca cations in the calcium silicate glass with the concentration of CaO in the range from 36 to about 48 weight% participate in the one-dimension ordering structure formation. The glass structure with such high CaO concentration should be represented by Figure 5(b), not Figure 5(a) or Figure 2. The proposed model's prediction about the calcium cations' medium-range order in the calcium silicate glass is supported by advanced neutron scattering experimental results as reported in the Journal Nature by P. H. Gaskell and colleagues more than thirty years ago [19,20].

4. Concluding Remarks

Based on the nanoflake model of silica glass, sodium silicate glasses are found to be structurally and chemically heterogeneous in the nanoscale. The glass structures cannot be accurately described by only a single graph. The glass structures change as the concentration of Na_2O in the system increases and need at least two graphs, such as Figure 5(a) and 5(b), to describe it fully. The proposed model may be extended to other binary and multiple component silicate glasses and can be verified against experimental data.

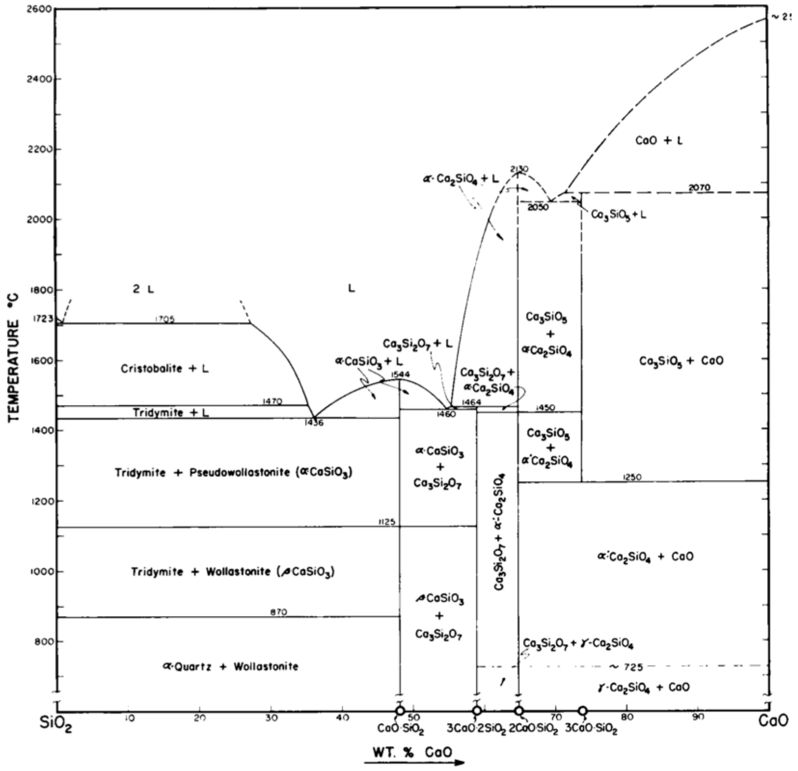


Figure 7. The SiO_2-CaO phase diagram.

The figure shows that as the CaO concentration increases to about 36 weight%, the liquidus temperature decreases to 1436°C. However, further increase in the CaO concentration causes the liquidus temperature to rise, and the corresponding crystal is the $CaSiO_3$. (Reproduced from Ref. 18)

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