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Statistical Mechanical Model for the Formation of Octahedral Silicon in Phosphosilicate Glasses

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Abstract

Unlike ambient pressure silicate glasses, some phosphosilicate glasses contain six-fold coordinated silicon (Si^6) units even when prepared at ambient pressure. The variation in the fraction of Si^6 with composition remains a topic of interest, both for technological applications of phosphosilicate glasses and for fundamental understanding of the glass structure. In this work, we use statistical mechanical modeling to predict the composition-structure relationships in Na_2O-P_2O_5-SiO_2 and CaO-P_2O_5-SiO_2 glasses. This is achieved by accounting for the enthalpic and entropic contributions to the interactions between each pairwise modifier ion and structural unit. The initial enthalpy parameters are obtained based on experimental structural data for binary Na_2O-SiO_2, CaO-SiO_2, Na_2O-P_2O_5, and CaO-P_2O_5 glasses, which can then be transferred to predict the structure of mixed former glasses. This approach has previously been used to predict the short-range structure of borosilicate and aluminoborate glass systems. However, here we show that the formation of Si^6 must be specifically included to make accurate predictions of the composition-structure relationships in phosphosilicate glasses. After incorporating the formation mechanism of Si^6 in the statistical mechanics model, we find an excellent agreement between model predictions and experimental data for Na_2O-P_2O_5-SiO_2 and CaO-P_2O_5-SiO_2 glasses.

Introduction

Phosphosilicate glasses have potential for various high-tech applications such as fiber lasers or fuel cells, and due to their good solubility in aqueous media and biocompatibility, they are mostly known for their bioactive properties for the regeneration of hard and soft tissue in the human body.[1,2] From a glass structure perspective, phosphosilicate glasses are especially interesting for the complex Si-P mixing and the presence of sixfold-coordinated silicon (Si^6) even when prepared at ambient pressure.[3,4] The high-coordinated silicon unit is typically limited to high-pressure crystals[5] and is not found in silicate glasses at ambient pressure.[6] Therefore, understanding the formation mechanism of Si^6 and the compositional dependence of its fraction in phosphosilicate glasses provide valuable insight for designing new functional glasses. This is important because octahedral Si has a vastly different influence on the network rigidity and thus macroscopic properties compared to tetrahedral Si.[7]

Phosphosilicate glasses are linked together through P and Si network formers that form the structural backbone and are connected through bridging oxygens (BOs). Network modifiers (such as Ca^{2+} or Na^+) typically break the backbone of the glass network by forming non-bridging oxygens (NBOs), but at the same time, the Si^6 units formed in phosphosilicate glasses require network modifying cations to be charge-balanced.[7,8] Hence, the addition of network modifiers may either decrease the network connectivity by forming NBOs or increase the network connectivity by inducing the formation of Si^6 units. In Si^6-rich phosphosilicate glass compositions, some evidence of five-fold coordinated silicon units (Si^5) has been obtained by ^{29}Si nuclear magnetic resonance (NMR) spectroscopy but at a very low concentration.[3] As such, we do not consider the Si^5 species in this work. Multiple studies have proposed different mechanisms for the formation of Si.[6] [3,7,9] The proposed mechanisms include (a) two oxygen atoms coordinating to the central Si without forming covalent bonds, (b) the formation of oxygen-triclusters, and (c) negatively charged Si^6 units charge-balanced by modifier cations. Of these assumptions, the formation of negatively charged Si^6 units appears most reasonable when considering the charges of the modifier ions balanced against the former units (-0.01 against +0.16).[7] That is, the negative charge on the Si^6 units in assumption (c) results in approximate charge stability in the phosphosilicate glasses. The formation mechanism of negatively charged Si^6 has been proposed to follow the chemical reaction shown in Figure 1.[7]

Previous studies found an increase in physical properties such as Vickers hardness and glass transition temperature (T_g) with the increase of Si^6 units, which arises from the increase in the number of topological constraints in the network.[9,10] As the topological constraints are a direct measure of the short-range glass structures, establishing a composition-structure model for this glass system would enable prediction of phosphosilicate glass properties directly from their composition.[11-15] The aim of this study is to develop such a composition-structure model. Recently, a statistical mechanics-based modeling approach has been applied to determine relative enthalpy barriers for modifiers to associate with the various network former units in binary modifier-former glasses,[16,17] and consequently to predict the compositional evolution of short-range structural units. In later work, the energy barriers found in binary M_1-F_1 and M_1-F_2 glasses (where M_n and F_n refer to specific network modifiers and formers, respectively) were used directly to calculate the structures in mixed M_1-F_1-F_2 ternary glasses.[18,19]

In these earlier cases, the structures found in the ternary glasses do not qualitatively differ from those found in the binary glasses. The Si^6 unit, however, has not been observed in binary silicate glasses synthesized at ambient pressure, and it is thus challenging to establish a statistical mechanics-based structural model for phosphosilicate glasses. In this work, we extend the statistical mechanical model to capture Si^6 formation in sodium and calcium phosphosilicate glasses by accounting for the chemical reaction shown in Figure 1. To this end, we here shed light on the requirements for the formation of Si^6 in phosphosilicate glasses and offer a model for predicting the structures of phosphosilicate glasses as a function of composition and thermal history.

2. Model

The statistical mechanical model used herein to predict the network modifier-former associations in mixed network former glasses was first proposed by Mauro[16,17,20] and later implemented and validated by Bødker *et al.*[21]. The model is based on the assumption that the probability for the initially added network modifier to interact with either network former species depends on the relative statistical entropy (i.e., the fraction of microstates consistent with the macrostate of each network former) and the relative enthalpic barrier for the modifier to break the bonds associated with each network former.

Considering the Na_2O-P_2O_5-SiO_2 system, the probability for sodium to associate with a phosphate unit depends on the statistical entropy of phosphate (i.e., the fraction of P_2O_5 to SiO_2) and the enthalpic energy barrier for this interaction relative to the enthalpic barrier of the sodium-silicate interaction. We can calculate the probability for each type of interaction using a Wallenius type non-central hypergeometric distribution function[22] by assuming that the energy barrier for a modifier to interact with the network former is constant regardless of the composition. The statistical entropy of each network former species does, however, change upon interactions with a modifier ion since a removed species is not replaced, thereby leading to hypergeometric statistics. We, therefore, implement an appropriate hypergeometric distribution to describe the evolution of network former species as a function of the modifier concentration. As the entropy of the system changes with composition, so does the probability for the modifier-former interaction, requiring a numerical solution to predict the structural evolution of network former species.

The specific type of non-central hypergeometric distribution incorporates a Boltzmann probability factor as,[23]

$$p_{i,\omega} = \frac{(g_i - n_{i,\omega-1}) e^{-\frac{H_i}{kT}}}{\sum_{j=1}^{M} \sum_{\omega=0}^{\omega-1} (g_j - n_{j,\omega-1}) e^{-\frac{H_j}{kT}}}, \tag{1}$$

where p_i is the probability of interaction i, ω is the modifier concentration, k is the Boltzmann constant, H_i is the energy barrier associated with species i, T is the temperature of the system, g_i is the degeneracy of species i and $n_{i,\omega}$ is the total fraction of species i that has already interacted at modifier concentration ω. In other words, the probability for a modifier to interact with a structure species i equals the fraction of that species at the modifier concentration ω weighted by the Boltzmann factor (scaling with H_i og T) relative to the sum of all species weighted by their individual Boltzmann factors. For each concentration step, the fraction $n_{i,\omega}$ of network former species i interacting with the modifier ion can be calculated from the probability of the interaction and its fraction at the previous concentration step ω-1. Then, that fraction is subtracted from the remaining amount of network forming species i at the next concentration, which is used to calculate the new probability, and so on. The application of Eq. (1) to predict the structure of binary and ternary oxide glasses has been described in detail elsewhere.[18,21]

The equilibrium constant K for the reaction shown in Figure 1 can be defined as,

$$K = \frac{[Si^6]\cdot[P^3]^2}{[Si^4]\cdot[P^2]^2}. \tag{2}$$

This equilibrium constant captures the relationship between the fractions of Si^6 units and P^2 units. However, studies[3,7,9] have reported data for Na_2O-P_2O_5-SiO_2 glasses containing Si^6 units but no Si^4 units, which, due to the uncertainty, would result in an infinitely large value of K in Eq. (2). While the value of K is likely large, the fraction of Si^4 units in those studies glasses must have been below the experimental detection limit. To enable accurate predictions of the fractions of Si^6 units in the present study, we therefore need to establish a correlation between Si^6 and P^3 that does not need to account for Si^4. To this end, previous studies have aimed at understanding and predicting the formation of Si^6 units. A study by Ren and Eckert[3] formulates empirical models for predicting the fraction of Si^6 units from composition based on the mechanism in Figure 1. Specifically, each Si^6 requires six P^3 units and two Na^+ (or one Ca^{2+}) to maintain charge balance in the glass. Their work can be rewritten to capture the chemical reaction in Figure 1 as,

$$\frac{[P^3]}{[SiO_2]}\cdot C_{Si^6} = \frac{[Si^6]}{[SiO_2]}, \tag{3}$$

where $[SiO_2]$ is the total concentration of silica in the glass and the fraction of P^3 and Si^6 can be calculated iteratively, given C_{Si6} is known. We note that Eq. (3) is only to be used when the two above requirements are fulfilled. Here, we will include the constant C_{Si6} in the model prediction as the only free parameter, while H_i values associated with P and Si structural units are established in binary phosphate and silicate glasses. When implementing Eq. (3) in the statistical mechanics-based model, it is only used to calculate the initial concentration of Si^6 units, after which the enthalpic and entropic contributions to the structural distribution are accounted for using Eq. (1).

3. Results and Discussion

3.1 Establishing interaction enthalpies for binary glass systems

The present model has previously been established for some binary phosphate[21] and silicate[24] glasses. For the purpose of this study, we have applied this approach to calcium silicate (Figure 2a) and calcium phosphate (Figure 2b) glasses. We note that parameters and glass compositions for sodium silicate and sodium phosphate glasses have already been established in previous work[21,24]. The model is established based on experimental ^{29}Si and ^{31}P magic angle spinning (MAS) NMR spectroscopy data from literature[25-28], and does not consider formation of Si^6 units in the binary silicate glasses in agreement with the experimental data (at ambient pressure). We find that the model captures the evolution of structural Q^n units in the binary glasses with the modifier concentration very well with the obtained H_i values as reported in Table 1. To obtain relative H_i values for the binary phosphate and silicate systems, T_g values are required as T_g is assumed to be the temperature where the structure stops rearranging. As such, it is the temperature that affects the entropic contribution in Eq. (1). Here, we extrapolate the T_g vs. composition data found in literature[25,29-31] using simple regression to estimate a T_g value for each modifier concentration step (ω).

The structural units in the Na_2O-P_2O_5 and CaO-P_2O_5 glasses undergo a step-like transformation from P^n to P^{n-1} (Figure 2b), with only two units simultaneously present at any composition. This has been suggested to be caused by the high-energy of the P=O bond found in P^3 units as the double bond can be conjugated with a P-O^- bond in the P^2 unit, and the latter has much lower energy than the P^3 unit.[32] Consequently, the system releases more energy by transforming a P^3 to a P^2 than by converting a P^2 to a P^1, which is captured accurately by the statistical mechanical model H_i parameters in Table 1. On the other hand, Si-O bonds in Si^4 units also hold more potential energy than Si-O bonds in Si^3 units due to the higher degree of constraint on the Si^4-O bond, but the difference between H_i values for Si^4 and Si^3 is low enough to ensure that modifiers will interact with Si^3 units and Si^4 units simultaneous. This allows for more than two species to be present simultaneously in silicate glasses.[33] Here, the enthalpic effect is described by ΔH (H_i-H_{i-1}) and the entropic effect governed by the number of units and T_g compete to control the structural distribution. The H_i values represent the enthalpic barriers for the reactions. For example, the P^2 to P^1 reaction releases 42.8 kJ/mol less energy than the P^3 to P^2 reaction, while the difference between Si^4 to Si^3 and Si^3 to Si^2 is only 14.1 kJ/mol. This results in a more entropically controlled structural distribution in the Na_2O-SiO_2 glass system than the Na_2O-P_2O_5 system, as reflected in Figure 2.

3.2 Statistical mechanical model of ternary phosphosilicate glasses without accounting for Si^6

The H_i values obtained by fitting the statistical mechanical model to binary oxide glasses have previously been used directly to calculate the structures of ternary borosilicate and aluminoborate glasses.[18,19] As the H_i values in Table 1 for silicate glasses are relative to that of the modifier-to-Si^4 interaction and the H_i values for the phosphate glasses are relative to that of the modifier-to-P^3 interaction, one additional parameter, $w_{Si/P}$, is required to relate the Si H_i values to the P H_i values. That is, a parameter is needed to inform the model with knowledge about the relative enthalpic preference for a modifier ion to interact with the silicate relative to the phosphate subnetwork.[18]

Figure 3a shows the model prediction of structural units in the Na_2O-SiO_2-P_2O_5 glass system as a function of the experimental structural data obtained from literature[3,7,9,34]. For these predictions, the H_i values are taken from Table 1, with only $w_{Si/P}$ as a fitting parameter. $w_{Si/P}$ is found to be 11.3, i.e., a modifier is ~11 times more likely to interact with a P^3 unit than a Si^4 unit, given the concentrations of those units are equal. For more detailed information on the fitting procedure and the use of a H_i scaling parameter, we refer to Ref[18]. Next, we use the $w_{Si/P}$ obtained in the Na_2O-SiO_2-P_2O_5 glass system and H_i values obtained in the binary CaO-P_2O_5 and CaO-SiO_2 glass systems (Table 1) to calculate the structural distribution in CaO-SiO_2-P_2O_5 glasses and make a comparison with experimental structural data from literature,[35-38] as shown in Figure 3b. That is, the prediction in Figure 3b is obtained without any fitting parameters as the model has already been trained on binary glasses for the H_i values and the Na_2O-SiO_2-P_2O_5 glasses for the $w_{Si/P}$ value. The compositions of the glasses used in Figure 3a and 3b are shown in the ternary diagrams in Figure 4a and 4b, respectively. In general, the smaller the concentration of sodium modifiers in the sodium phosphosilicate glasses, the higher the fraction of high-coordinated silicon units.[3,7,9]

As seen in Figure 3a, the model is not able to capture the Si^6 units as these do not exist in the binary silicate glasses that the H_i values are based established from. Additionally, the model does not accurately capture the distribution of other structural units in the CaO-SiO_2-P_2O_5 glass system (Figure 3b). Therefore, the chemical reaction of Si^6 formation in phosphosilicate glasses must be captured in the statistical mechanical model to predict the structural distribution of all the species correctly.

3.3 Statistical mechanical model of ternary phosphosilicate glasses that accounts for Si^6

As such, we only used two fitting parameters (C_{Si6} and $w_{Si/P}$) to predict the structural distribution of Na_2O-SiO_2-P_2O_5 glasses, while the H_i values were taken from Table 1. We choose the Na_2O-SiO_2-P_2O_5 glass family as it contains a relatively high fraction of Si^6 units in the glass-forming region compared to other phosphosilicate systems. The excellent agreement between model prediction and experimental data is shown in Figure 5a, where all structural units are captured by the model. The fitted value of C_{Si6} is found to be 0.2, indicating a high fraction of Si^6 units at low modifier concentrations, as also shown in previous studies.[3,9] Next, we use the established parameters C_{Si6} and $w_{Si/P}$ as well as H_i values for CaO-SiO_2 and CaO-P_2O_5 to predict the structural distribution in CaO-SiO_2-P_2O_5 glasses. Comparison to experimentally obtained values structure data from literature[35-38] in Figure 5b shows a much-improved fit compared to Figure 3b. We note that this improvement is observed although the CaO-SiO_2-P_2O_5 glasses do not contain high-coordinated silicon units. This is because we capture the Si^6 forming chemical reaction, which is also essential when capturing glass structure even at high modifier concentrations in phosphosilicate glasses, where no Si^6 is present. When combining Eq. (3) to capture the fraction of Si^6 units with the statistical mechanics-based model of Eq. (1), the temperature dependence of the fraction of Si^6 units is also captured, which may help to explain the good fit of the data in Figures 5a and 5b.

Our results show that the statistical mechanical modeling approach can predict structural distributions in oxide glasses with any components, as long as the inherent chemical interactions, enthalpy values and T_g values are known. H_i values are transferrable between glass systems, i.e., a relatively small database of H_i values is sufficient to capture the short-range structure of many glass systems. Here, we have shown that even abnormal former-former interactions can be captured by the model and with the addition of Si^6 formation, the accuracy of the model has been increased in any glass system simultaneously containing phosphate and silicate species. In future work, it would be interesting to incorporate our improved compostion-structure model into existing structure-property models, such as those based on topological constraint theory, for phosphosilicate glasses[7]. This should allow for a quantitative prediction of the variation in glass properties with the fraction of Si^6 units[9,10].

4. Conclusions

We have shown that a structure model based on the Boltzmann distribution can be used to predict the structure of ternary phosphosilicate glasses by capturing the formation of sixfold-coordinated silicon units. Reaction enthalpies for modifiers to interact with different structural species within the glass-forming melt are established in binary silicate and phosphate glasses by fitting the statistical mechanical model to NMR data from literature. Using these values, we have applied the model to predict the structural evolution in sodium phosphosilicate glasses with only one free parameter, $w_{Si/P}$, to account for the relative propensity for the sodium modifier to interact with either the silicon or phosphorous part of the network. We find that this approach is insufficient for capturing the high-coordinated silicon units, and we have incorporated a proposed Si^6 formation mechanism in the statistical mechanical model to capture the formation of these units. This introduced another parameter, C_{Si6}, describing the equilibrium between sixfold-coordinated silicon and P^3. With the C_{Si6} and $w_{Si/P}$ parameters established in the sodium phosphosilicate system, we finally use the model to predict the structural evolution in calcium phosphosilicate glasses without any free parameters.

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Tables

Table 1: Relative enthalpy (H_i) values for modifier-former interactions. The values have been obtained when fitting the statistical mechanical model to structural data from literature[25-28,33,39-46] for binary phosphate and silicate glasses. RMSE is provided to compare the quality of the fits.

Glass System	Na_2O-P_2O_5	CaO-P_2O_5	Na_2O-SiO_2	CaO-SiO_2
H_4 (kJ/mol)	-	-	0	0
H_4-H_3 (kJ/mol)	0	0	14.1	5.0
H_2-H_3 (kJ/mol)	42.8	24.7	22.9	15.7
H_1-H_3 (kJ/mol)	74.9	64.5	27.1	30.5
RMSE	0.94	0.79	1.26	2.63

Figures

Figure 1: Proposed reaction for the formation of sixfold-coordinated silicon units in phosphosilicate glasses.[7] Here, the Si^6 unit is assumed to be negatively charged and must be charge stabilized by modifier ions, i.e., the formation of one Si^6 unit occurs instead of the formation of two P^2 units.

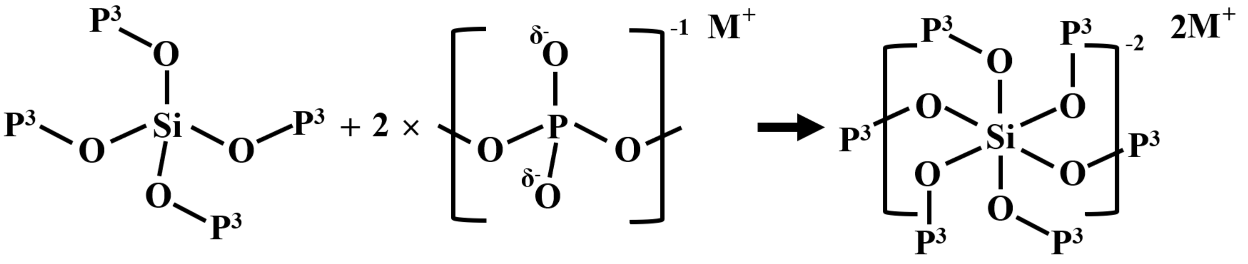


Figure 2: Fraction of structural units in binary (a) sodium silicate and (b) sodium phosphate glasses as a function of modifier content. Solid lines model predictions using Eq. (1) and the experimental data from literature are shown as symbols[25-28,41,42].

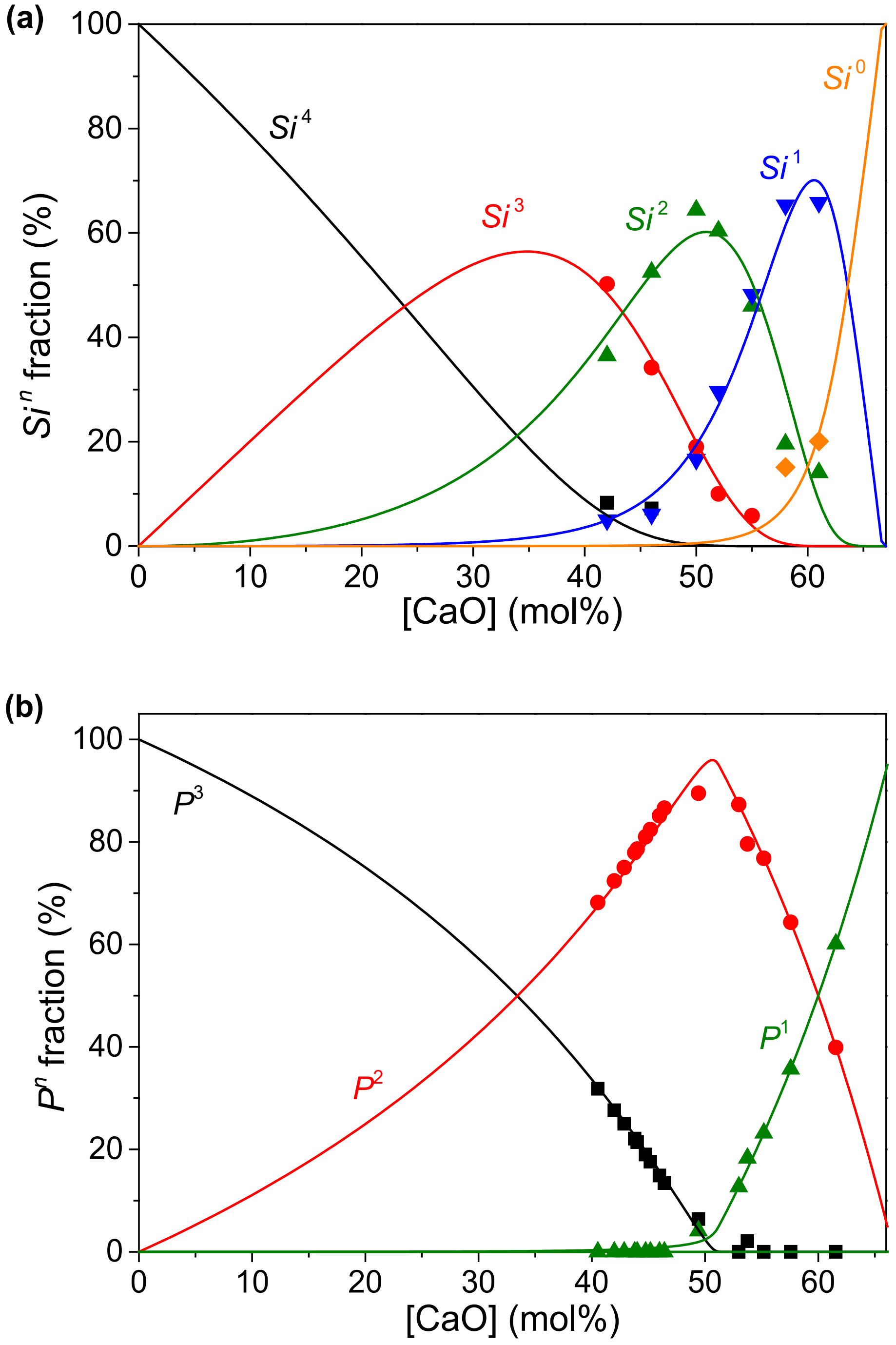


Figure 3: Comparison of model predictions and experimental data for the structural units in (a) Na_2O-SiO_2-P_2O_5 and (b) CaO-SiO_2-P_2O_5 glasses. The model predictions are based on enthalpy values established in the binary silicate and phosphate glasses, as reported in Table 1. The experimental data are from ^{29}Si and ^{31}P MAS NMR spectroscopy[3,7,9,34-38].

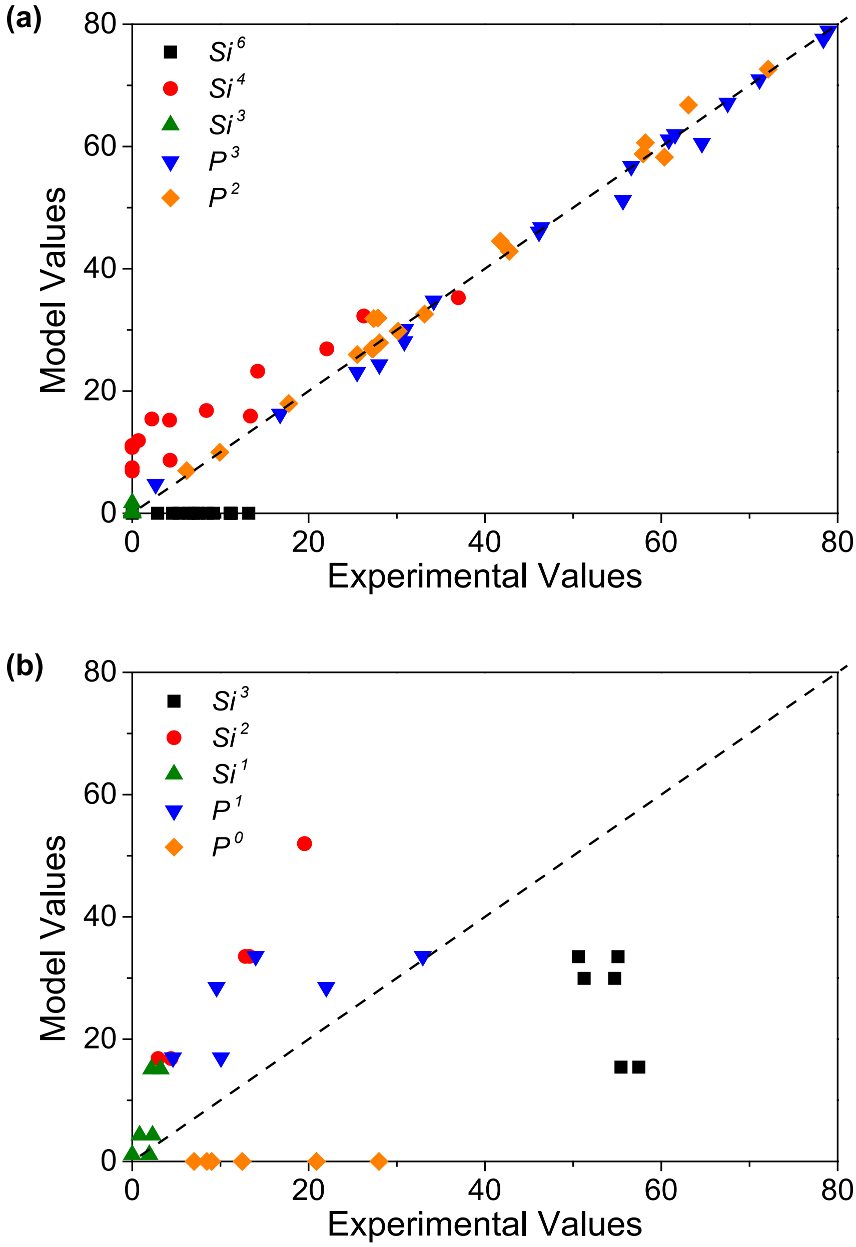
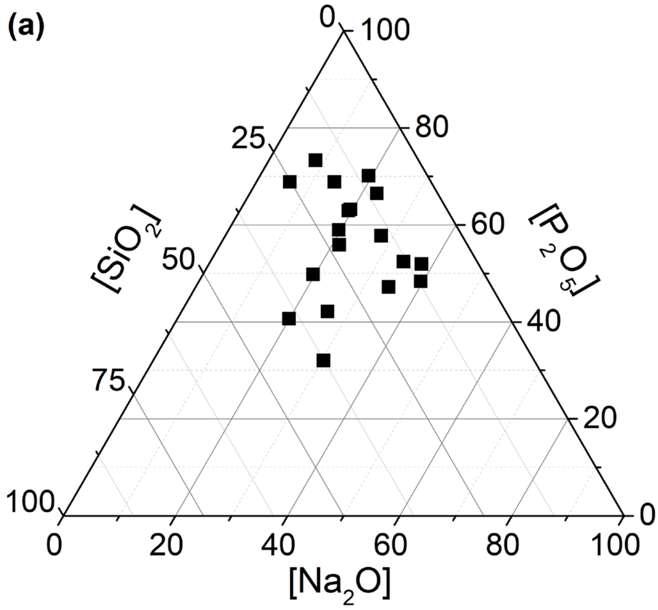


Figure 4: Ternary diagrams showing the compositional space (in mol%) of the (a) Na_2O-P_2O_5-SiO_2 and (b) CaO-P_2O_5-SiO_2 glasses from literature[3,7,9,34-38].



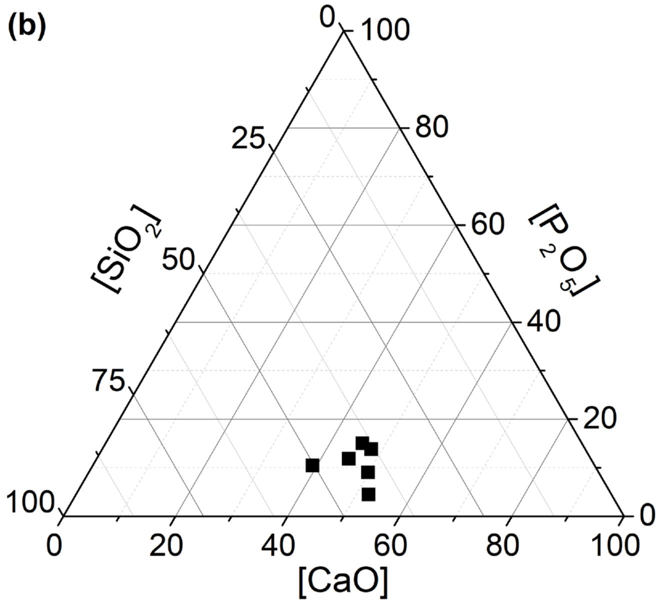


Figure 5: Comparison of model predictions and experimental data for the structural units in (a) Na_2O-SiO_2-P_2O_5 and (b) CaO-SiO_2-P_2O_5 glasses. The model predictions are based on enthalpy values established in the binary silicate and phosphate glasses as reported in Table 1 and the Si^6 formation captured by Eq. 2. The experimental data are from ^{29}Si and ^{31}P MAS NMR spectroscopy[3,7,9,34-38].