MOLECULAR DYNAMICS OF $33Na_2O.20TiO_2.47SiO_2$ MELT AND GLASS

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Received February 13, 1997.

Results of molecular dynamics (MD) simulation of title glass (T = 500 K) and melt (T = 1500 K) are reported for two sizes of a basic computational cell, corresponding to the density of 1900 kg m^{-3} and 2000 kg m^{-3}, respectively. Partial cation-anion pair radial distribution functions (RDFs) and corresponding mean co-ordination numbers describing the short range - nearest neighbour order, were found to be almost insensitive to the studied density change at both considered temperatures. Silicon was found four- and five-coordinated by oxygen, while the co-ordination numbers 4, 5 and 6 were detected for the Ti/O co-ordination on the basis of direct polyhedra analysis. The distribution of TiO_x (x = 4,5,6) coordination polyhedra was sensitive to the density at both considered temperatures. The increasing density shifts this distribution towards the five-coordination. The abundance of five coordinated titanium and silicon is positively correlated with temperature.

INTRODUCTION

Titania bearing silicate melts and glasses play an important role in both the igneous petrology and the glass technology. From the later point of view, the low values of thermal expansion coefficient, optical, electrical and durability properties have to be mentioned [1]. The difficulties in the experimental study of the structure of the titania bearing silicate melts [2-3] designate these systems as ideal objects for molecular dynamics (MD) study. However, despite of this fact, such MD calculations rarely occur in the literature. Among them, the MD study of amorphous titanium silicate of Rosenthal and Garofalini [4] has to be mentioned, where the empirical pair potential function (PPF) of the Born-Mayer-Huggins (BMH) type was developed for titanium cation. The results obtained in that work indicate that at low concentrations (< 10 mol.% TiO_2) titanium atom is mainly tetrahedraly coordinated in the bulk silica. At higher TiO_2 concentrations the coordination of the Ti atom increases. These MD results are consistent with EXAFS data of bond lengths and with the coordination numbers of Ti in titanium silicate glasses [5].

The three-component Na_2O-TiO_2-SiO_2 system was treated in the MD simulations of Iwamoto et al. [6] in order to elucidate the influence of TiO_2 on the structure of sodium silicate glasses and melts. The BMH-type PPFs were used with the unrealistic size parameter for Si^{4+}. The radial distribution functions calculated for $25Na_2O.28TiO_2.47SiO_2$ glass were in the good agreement with the results obtained from time-of-flight pulsed neutron scattering experiments. The most part of Ti^{4+} ions were in the 4-fold coordination with oxygen, whilst the rest of Ti^{4+} ions were 6-fold coordinated. The frequency spectrum (i.e. the density of vibrational states - DOS) of the glass obtained from the MD simulation was in the good agreement with the Raman spectrum [6].

These few works [4,6] illustrate the possibilities of MD simulations based on the simple empirical pair-wise BMH-type PPFs. We intend to perform in our future work MD simulations of a series of disilicate glass compositions in whose the equimolar substitution of SiO_2 with TiO_2 takes place. The structure of these glasses was studied by Raman spectroscopy in the excellent work of Mysen and Neuville [3]. Some questions concerning the Ti/O coordination are still open, giving such the opportunity for theoretical methods in the structural investigation of titania bearing silicate glasses. The main aim of the present work is to estimate the influence of the pressure (i.e. the size of the computational box) on the obtained structure, namely on the first (cation/oxygen) and the second (cation/cation) co-ordination spheres.

METHOD OF CALCULATION

The MD simulated system consisting of 900 ions (200 Na^+ + 60 Ti^{4+} + 140 Si^{4+} + 500 O^2) was placed into a cubic computational box subject to periodic boundary conditions. The volume of the computational box was adjusted to yield near zero (less than 10 kbar) MD pressure at 2000 K. The density corresponding to such volume of the computational box was 2000 kg m^{-3}. The interionic potentials, V_{ij}, were calculated using Born-Mayer-Huggins (BMH) type pair potential function (PPF)

$$V_{ij} = B_{ij} \exp\left(\frac{-r_{ij}}{\rho} \right) + \frac{e^2 z_i z_j}{4\pi\varepsilon_O r_{ij}} , \qquad (1)$$

where

$$B_{ij} = b(1 + z_i / n_i + z_j / n_j) \exp\left(\frac{\sigma_{ij}}{\rho} \right), \qquad (2)$$

r_{ij} is the distance between the i-th and j-th ion, z_i is the ionic charge in the units of the electron charge e, n_i is the number of valence shell electrons (n_i = 8 for Na^+, Ti^{4+}, Si^{4+} and O^{2-}), $b = 0.338 \times 10^{-19}$ J and ρ = 29 pm are empirical constants and σ_{ij} is the distance parameter characterizing the ionic radius. The additive condition

$$\sigma_{ij} = (\sigma_{ii} + \sigma_{jj}) / 2 \qquad (3)$$

was applied. The values for σ_{ii} were taken from the work of Soules [7] for the Na^+ (234 pm), Si^{4+} (230 pm) and O^{2-} (284 pm) ions and from the work of Rosenthal and Garofalini [4] for the Ti^{4+} (250 pm) ion. Computation time step of 1 fs was chosen in the correspondence with the value of the smallest vibration period, τ, calculated for isolated anion-cation pairs ($\tau(Na^+O^{2-})$ = 21 fs, $\tau(Ti^{4+}O^{2-})$ = 21 fs, and $\tau(Si^{4+}O^{2-})$ = 18 fs).

The simulation started from a random configuration at 6000 K and the system was equilibrated during 20 000 time steps (i.e., 20 ps). The cooling procedure comprised a sudden reduction of the kinetic energy of all atoms followed by numerical control at the required temperature (2000 time steps), and then by equilibration and measuring period (18 000 time steps). The successive temperature steps were 4000, 3000, 2500, 2000, 1750, 1500, 1250, 1000, 750 and 500 K, respectively.

The MD calculations were carried out employing a modified version of MDIONS program [8] where Ewald summation method is used for the calculation of Coulombic interactions.

For the purpose of coordination description, the algorithm for direct polyhedra construction has been adopted, as described by Brostow et al. [9].

RESULTS AND DISCUSSION

The short range order of the studied melt/glass is described by the cation-anion partial pair RDFs visualized in figure 1. Only the results obtained for the density of 2000 kg m^{-3} are plotted in figure 1 because the results obtained for the density of 1900 kg m^{-3} are almost the same. It can be seen that the regularity of the short range order increases with decreasing temperature. The mean pressure values, corresponding to the particular density and temperature, are summarized together with corresponding standard deviations in table 2. Using the method of generalized coordination vectors described in [10], the distribution of SiO_x and TiO_x coordination polyhedra can be evaluated (table 1). The enhanced five-coordination of silicon atom, observed mainly at elevated temperature, may be considered as the artifact of using the direct polyhedra tessellation, which can include also the more distant oxygen anions. Except of this fact, it can be concluded, that the silicon-oxygen nearest neighbor order is relatively invariant to the density change examined. The distribution of TiO_x coordination polyhedra is significantly broader than those of SiO_x ones. The dominant role plays the Ti/O five-coordination, the number of four-coordinated titanium cations represents about one half of the five-coordinated ones, and the six-coordinated species may be considered as defects but with the significant abundance. From table 1. it can be deduced, that the abundance of five-(four-) coordinated TiO_x species is positively (negatively) correlated with the density at both temperatures.

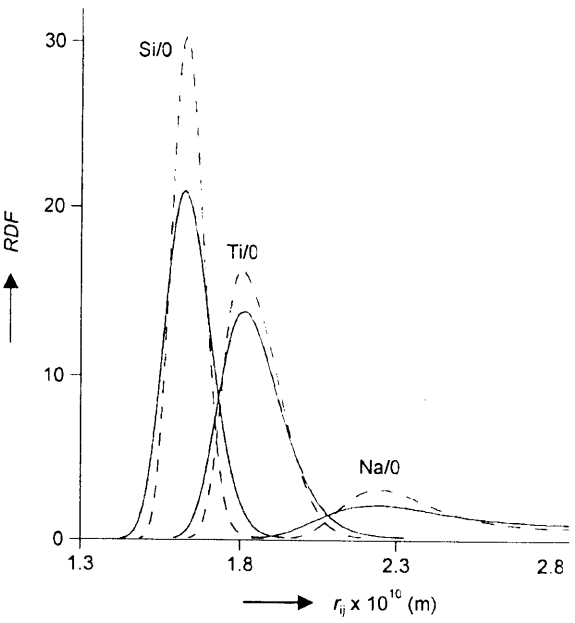

Figure 1. The cation-anion pair RDFs at the density of 2000 kg m^{-3} (full line - 1500 K, dashed line - 500 K).

Table 2 summarizes the mean Si/O and Ti/O co-ordination numbers determined from both, the direct polyhedra tessellation, and from the integration of corresponding partial pair RDFs. The density and temperature invariance of Si-O short range order is strongly expressed by both used methods of the mean co-ordination number evaluation (table 2). However, the difference of 0.1 between these results indicate the above mentioned capability of the direct polyhedra to embrace more distant oxygen anions.

The temperature influence on the next nearest neighbor structural features can be seen from the cation-

Table 1. The distribution of titanium/oxygen and silicon/oxygen coordination numbers determined from direct polyhedra.

T (K)	ρ (kg m^{-3})	% SiO4	% SiO5	% TiO4	% TiO5	% TiO6
500	1900	94	6	37	57	6
500	2000	89	11	27	67	6
1500	1900	87	13	30	62	8
1500	2000	86	14	25	70	5

Table 2. The mean Si/O and Ti/O coordination numbers determined from the direct polyhedra (-d.p.) and from the partial pair radial distribution functions (-RDF), and the mean pressure value together with the standard deviation.

T (K)	ρ (kg m^{-3})	Si/O-d.p.	Si/O-RDF	Ti/O-d.p.	Ti/O-RDF	*p* (kbar)
500	1900	4.1	4.0	4.7	4.6	-9 ± 2
500	2000	4.1	4.0	4.8	4.7	-5 ± 2
1500	1900	4.1	4.0	4.8	4.6	-3 ± 4
1500	2000	4.1	4.0	4.8	4.7	1 ± 4

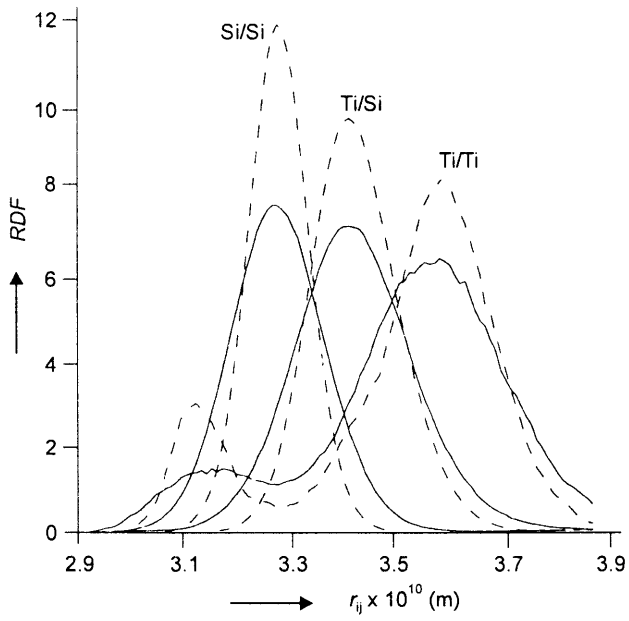

Figure 2. The partial pair RDFs describing the mutual Ti^{4+}, Si^{4+} arrangement at the density of 2000 kg m^{-3} (full line - 1500 K, dashed line - 500 K)

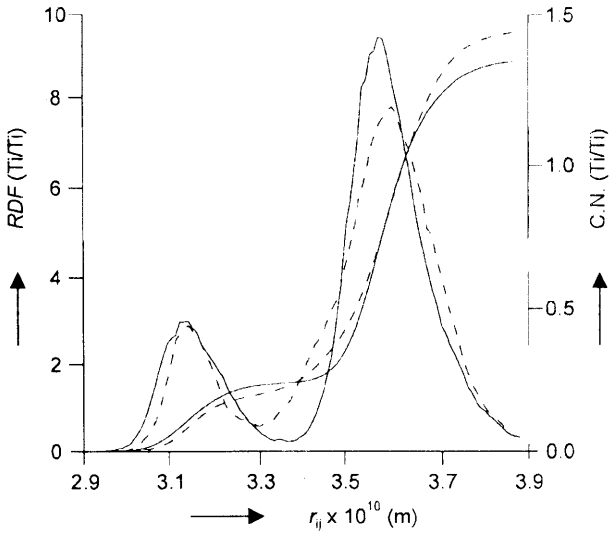

Figure 3. The dependence of Ti^{4+}-Ti^{4+} RDFs and co-ordination numbers (C.N.) on the density at 500 K (full line - 1900 kg m^{-3}, dashed line - 2000 kg m^{-3}).

cation partial pair RDFs plotted in figure 2 at the density of 2000 kg m^{-3}. As in the case of the cation-anion RDFs, the structure of glass is more regular than those of the melt. Unlike the nearest neighbor ordering, the significant density influence on the next nearest cation-cation neighbour structure was found. This fact is illustrated for the case of Ti^{4+}-Ti^{4+} pair in figure 3. Besides the RDFs, the radial dependence of Ti/Ti coordination number is also plotted in figure 3. The significant bimodality of RDF indicate two distinct mutual ordering of TiO_x polyhedra via the Ti-O-Ti bridges, perhaps the edge sharing (co-ordination number ≈ 0.3), and the corner sharing (co-ordination number ≈ 1.4).

CONCLUSIONS

The short range nearest neighbor order was found to be almost insensitive to the studied density change at both considered temperatures. Silicon atom is mainly four-coordinate by oxygen atoms with small amount of defect five-coordinated species. The co-ordination numbers 4 and 5 are dominant for Ti/O co-ordination. The distribution of TiO_x (x = 4, 5, 6) co-ordination polyhedra is sensitive to the density value at both considered temperatures. Increasing density shifts this distribution towards the five-coordination. The abundance of five coordinated titanium and silicon is positively correlated with temperature.

Acknowledgement

This work was supported by the Slovak Grant Agency for Science, Project no. 1171/96 and 95/5195/204.

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Submitted in English by the authors.

MOLEKULOVÁ DYNAMIKA TAVENINY A SKLA SO ZLOŽENÍM $33Na_2O.20TiO_2.47SiO_2$

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Metódou molekulovej dynamiky (MD) sa simulovala štruktúra skla (teplota 500 K) a taveniny (teplota 1500 K) so zložením $33Na_2O.20TiO_2.47SiO_2$. Výpočty sa uskutočnili pre dve hustoty simulovaného systému. Hustota 2000 kg m^{-3} zodpovedá nulovému MD tlaku pri teplote 2000 K a hustota 1900 kg m^{-3}, pri ktorej je tlak MD vyšší, sa zvolila na posúdenie vplyvu tlaku na základné štruktúrne charakteristiky simulovaných systémov.

Ukázalo sa, že parciálne párové radiálne distribučné funkcie (RDF) párov kation - anión ako aj príslušné koordinaèné čísla opisujúce usporiadanie na krátku vzdialenosť nie sú citlivé na skúmanú zmenu tlaku pri oboch uvažovaných teplotách. Na základe analýzy koordinácie metódou priamych polyédrov sa zistilo, že kremík je hlavne štvorkoordinovaný kyslíkom s minoritným výskytom päťkoordinácie. V prípade koordinácie titánu kyslíkom sa našli koordinačné čísla 4, 5 a 6. Relatívne zastúpenie jednotlivých koordinaèných čísiel bolo závislé od hustoty pri oboch uvažovaných teplotách, pričom vyšší tlak posúva túto rovnováhu smerom k päťkoordinácii. Výskyt päťkoordinovaného kremíka a titánu je pritom pozitívne korelovaný s teplotou.