



This is an electronic reprint of the original article. This reprint may differ from the original in pagination and typographic detail.

Santoso, Imam; Sibarani, David; Hidayat, Taufiq; Zulhan, Zulfiadi; Sukhomlinov, Dmitry; Chen, Min; Klemettinen, Lassi; Taskinen, Pekka; Lindberg, Daniel; Jokilaakso, Ari **Phase equilibria of the Na₂O-TiO₂-SiO₂ system between 900 and 1600°C in air**

Published in: Journal of the American Ceramic Society

DOI: 10.1111/jace.19845

Published: 01/09/2024

Document Version Publisher's PDF, also known as Version of record

Published under the following license: CC BY-NC-ND

Please cite the original version:

Santoso, I., Sibarani, D., Hidayat, T., Zulhan, Z., Sukhomlinov, D., Chen, M., Klemettinen, L., Taskinen, P., Lindberg, D., & Jokilaakso, A. (2024). Phase equilibria of the Na O-TiO -SiO system between 900 and 1600°C in air. *Journal of the American Ceramic Society*, *107*(9), 6307-6322. https://doi.org/10.1111/jace.19845

This material is protected by copyright and other intellectual property rights, and duplication or sale of all or part of any of the repository collections is not permitted, except that material may be duplicated by you for your research use or educational purposes in electronic or print form. You must obtain permission for any other use. Electronic or print copies may not be offered, whether for sale or otherwise to anyone who is not an authorised user.

RESEARCH ARTICLE



Ournal

Phase equilibria of the Na_2O -Ti O_2 -Si O_2 system between 900 and 1600°C in air

Imam Santoso^{1,2} David Sibarani² | Taufiq Hidayat¹ | Zulfiadi Zulhan¹ | Dmitry Sukhomlinov² Min Chen² Lassi Klemettinen² | Pekka Taskinen² Daniel Lindberg² | Ari Jokilaakso²

¹Department of Metallurgical Engineering, Faculty of Mining and Petroleum Engineering, Institut Teknologi Bandung, Bandung, Indonesia

²Department of Chemical and Metallurgical Engineering, School of Chemical Engineering, Aalto University, Espoo, Finland

Correspondence

Imam Santoso, Department of Metallurgical Engineering, Faculty of Mining and Petroleum Engineering, Institut Teknologi Bandung, Bandung, Indonesia. Email: imam.santoso@itb.ac.id

Funding information

Institut Teknologi Bandung; Aalto University from Business Finland and the Academy of Finland, Grant/Award Number: #341404 Abstract

The Na₂O-SiO₂-TiO₂ system is important for the glass, ceramic, and metallurgical industries. Its features provide information on the composition and melting temperature to be utilized during the production of glass and ceramic and during the processing of TiO₂-bearing material in the metallurgical industry. The liquidus temperatures between 900 and 1600°C in the ternary system at saturation of solid SiO₂, TiO_2 , $Na_2Ti_6O_{13}$, Na_2SiTiO_5 , and $Na_2Ti_3O_7$ were measured using the equilibration-quenching energy-dispersive X-ray spectroscopy/Electron Probe Microanalyzer technique. A wide range of liquidus compositions were obtained with Na₂O between 0 and 41.7 mol% in the SiO₂and TiO₂-rich regions. The present study provides liquidus data at 1500 and 1600°C for the first time. Liquidus temperatures at various double saturations were also obtained in the present investigation to determine univariant lines in the phase diagram. The present experimental data were compared with previous investigations and computed phase diagrams. The data obtained in the present investigation can be employed to optimize the thermodynamic properties and phase diagrams of the Na₂O-SiO₂-TiO₂ system.

KEYWORDS ceramics, phase diagram, slag, titania glass

1 | INTRODUCTION

The Na₂O-SiO₂-TiO₂ system is vital for the glass and ceramic industries and metallurgical applications. One of the factors determining the success of the melting and annealing process during soda silica-titania glassmaking is the understanding of Na₂O-SiO₂-TiO₂ phase diagrams. Recently, the Na₂O-SiO₂-TiO₂ system has attracted increasing attention for many investigations in glass and

ceramic technology and science. Na₂O-SiO₂-TiO₂ is the parent mixture in producing infrared glasses, with the addition of rare earth oxides, for example, La₂O₃ and Y_2O_3 .¹ TiO₂ doping of glass, such as sodium borosilicate,² can improve its chemical durability by reinforcing the glass structure. The addition of TiO₂ to soda-lime glass can improve the thermal expansion and refractive index^{3,4} of the glass. In extractive metallurgy, soda is added to the smelting process to control the viscosity and remove

This is an open access article under the terms of the Creative Commons Attribution-NonCommercial-NoDerivs License, which permits use and distribution in any medium, provided the original work is properly cited, the use is non-commercial and no modifications or adaptations are made.

ournal

the impurities as slag.^{5,6} Na₂O fluxing in the form of Na₂CO₃ can improve the recovery and kinetics of iron separation from SiO₂-Na₂O-TiO₂ slag that is titania-rich during the carbothermic reduction of ilmenite.^{7,8} The formation of soluble sodium compounds is crucial in numerous metal extraction processes.^{9,10} In the extraction of vanadium from titania-rich slag, the aim is to form sodium aluminosilicate, which can be leached to separate vanadium and titanium from impurities. Therefore, a complete mapping of areas where there is a fully molten liquid or a liquid saturated with stable compounds at a specified temperature is vital for glass synthesis and slag formation in the glass and metallurgical processes. This information can be derived from the phase assemblages in the Na₂O-SiO₂-TiO₂ diagram. However, the reported phase diagrams of the Na₂O-SiO₂-TiO₂ system are very limited, and mostly based on the study of Glasser and Marr.¹¹

They¹¹ investigated the Na₂O-SiO₂-TiO₂ system using melting, quenching, and petrographic methods. The glass samples at a specific composition for the melting and guenching experiments were prepared from Na_2CO_3 , SiO₂ and TiO₂ mixtures. Each mixture was melted in the targeted conditions and quenched. The chemical composition analyzed before and after preparation using the atomic absorption method indicated that Na₂O was evaporated at high temperatures. The glass samples were then heated and quenched to study the phase equilibria. The phase assemblages in the quenched samples were examined using optical microscopy. It was reported that, after remelting the glass between 1200 and 1300°C for a certain period, the evaporation of Na₂O was significant. Through this method, the evaporation of soda most likely affected the composition at liquidus temperature, resulting in the observed liquidus composition with a lower Na₂O content than that calculated in the initial glass mixture. Furthermore, when using this method, the liquidus temperature can only be estimated from the composition of the prepared initial glass mixture, including the composition at 900-1400°C reported by Glasser and Marr.¹¹ Therefore, this system needs to be reinvestigated with a more reliable experimental technique that can control the evaporation and initial mixture problems.¹²⁻¹⁴

Glasser and Marr¹¹ reported a ternary compound of Na₂TiSiO₅ that melts congruently at 965°C, and Na₂TiSi₄O₁₄, Na₂Ti₂Si₂O₇, and Na₂TiSi₂O₇ which have incongruent melting points of 919, 919, and 852°C, respectively. The reported liquid compositions at these solid saturations and the corresponding primary phase fields were drawn in the ternary diagram. Nevertheless, the investigation extended only up to 1400°C, whereas for metallurgical applications, information at higher temperatures is needed since, for example, the reduction process involving titania-bearing slag operates from 1500 to 1600°C. Therefore, the phase equilibrium data at 1500 and 1600°C are needed. In addition, liquidus contours in the ternary diagram reported.¹¹ especially at low SiO_2 concentrations, were only estimated. They are presented by a dashed line in the diagram. Thus, the composition measurements of the liquid phase at low concentrations of SiO_2 and multiple solid phase saturation are required to provide comprehensive phase diagrams.

Hamilton and Cleek¹⁵ measured the liquidus temperature of the Na₂O-TiO₂-SiO₂ system by temperature gradient technique. The liquidus data were obtained with the Na₂O and TiO₂ contents in the glass varying from 0 to 35 mol% and from 0 to 45 mol%, respectively, at SiO₂, Na₂Si₂O₅, Na₂SiO₃, and Na₂SiTiO₅ saturations. They found that in the mixture containing 25 to 35 mol% Na₂O, the increase in the TiO₂ will increase the liquidus temperature of the glass. The maximum liquidus temperature they reported is only up to 1200°C. Vanis et al.¹⁶ measured the liquidus temperatures of the Na₂TiO₂–Na₂SiTiO₅ joint by using petrographic and DTA methods and reported an eutectic temperature of around 800°C.

Thermodynamic assessment of binary Na₂O-TiO₂ and SiO₂-TiO₂ systems have been undertaken by several investigations and different melt models were employed. Kirschen et al.¹⁷ modeled the excess properties of TiO₂-SiO₂ melts by using the Margules type model and optimized the system by using a linear programming technique. They¹⁷ reported the miscibility gaps in the system with the critical temperature of 2612°C. The sub-regular model was employed by Kirillova et al.¹⁸ to illustrate the SiO₂-TiO₂ melts. They¹⁸ reported computed phase diagram with the miscibility gap at a critical temperature of 2143°C only, far below the temperature reported by Kirschen et al.¹⁷ Modified Quasi-Chemical model was employed by Eriksson and Pelton,¹⁹ and Wu et al.²⁰ to describe molten oxide and least square method was employed for optimization. Binary phase diagrams of Na₂O-TiO₂ and Na₂O-SiO₂ computed and reported by Eriksson and Pelton,19 and Wu et al.²⁰ respectively. Kang et al.²¹ used the Modified Quasi-Chemical model to describe the molten SiO₂-TiO₂-Ti₂O₃ system. It is clear that the binary systems of Na₂O-TiO₂, SiO₂-TiO₂ and Na₂O-SiO₂ have been assessed.¹⁷⁻²¹ However, there is no report in the literature about the modeling and optimization of the Na₂O-SiO₂-TiO₂ system. Therefore, a detailed investigation to generate new liquidus data of the Na₂O-SiO₂-TiO₂ system, in addition to the data by Glasser and Marr^{,11} is advantageous for re-optimizing the existing model.

2 | METHODS

In the present investigation, the equilibration-quenching energy-dispersive X-ray spectroscopy/Electron Probe Microanalyzer (EDS/EPMA) technique was employed.

TABLE 1 Chemicals employed in the present study.

No.	Chemicals	Supplier	Purity (wt%)
1	Na_2CO_3	Sigma Aldrich	99.9
2	SiO ₂	Umicore	99.9
3	TiO ₂	Sigma Aldrich	99.8



FIGURE 1 Schematic arrangement of the sample holder.

The temperature intervals were specified for investigating the isothermal sections. The compositions of the equilibrium phases were measured directly from the quenched samples. The final phase compositions were determined using EDS/EPMA analyses. The initial batch compositions were pre-determined from preliminary estimates of the phase assemblages and their compositions at the target temperatures. By applying the quenching technique, solid phases at high temperatures were retained and the liquid phase was transformed into glass or a microcrystalline phase at room temperature.

2.1 | Preparation of the samples

The high-purity TiO_2 , Na_2CO_3 , and SiO_2 chemicals listed in Table 1 were employed in the present investigation. The precursors were weighed and mixed in an agate mortar and then pressed using a 5 MPa pressing tool to form 0.15 g pellets. The samples were then placed in platinum crucibles. A schematic design of the sample holder is presented in Figure 1. The behavior of Na_2O during the experiment needs to be understood to obtain the targeted paths in the final equilibrium condition. An excess of Na_2O in the initial mixture was crucial to compensate for Na_2O evaporation. Although Na_2O evaporated and changed the initial bulk composition and tie line, the final liquidus composi-



FIGURE 2 Schematic arrangement of the furnace.

tion followed the same liquidus line, that is, the different tie lines ended up in the same liquidus line.

2.2 | High-temperature isothermal-equilibration experiments

The samples were equilibrated inside a vertical tube furnace (Nabertherm RHTV 120-150/18, MoSi₂ heating elements). The tube of the furnace was made of dense sintered (impervious) alumina. The samples were hung on a platinum wire in the hot zone of the furnace. A brass head with two holes for two small alumina tubes was installed on the top of the furnace, one tube for the sample wire and another for the external thermocouple which measured the sample temperature. A water-cooling system was installed at the top and bottom of the furnace. The external thermocouple was a calibrated S-type made from Pt and Pt-Rh wires (Johnson-Matthew). The temperature uncertainty was approximately \pm 3°C. The thermocouple was connected to 2010 DMM and 2000 DMM Keithley multimeters (Keithley Instruments, USA) for the hot and cold junctions, respectively, and computer software to record the temperature of the sample continuously every 5 s. The bottom of the furnace was open to the air to obtain an oxygen partial pressure of 0.21 atm so that the titanium was oxidized into Ti4+ in all phases during the equilibration process.²² A schematic diagram of the furnace arrangement is presented in Figure 2.

TABLE 2 Standards used in the Electron Probe Microanalyzer (EPMA) measurements.

Element	0	Na	Si	Ti
X-ray line	Κα	Κα	Κα	Κα
Standard material	Olivine	Tugtupite	Quartz	Rutile

equilibration at 900°C two days of experiments were performed to guarantee the reaction had reached equilibrium, whereas three hours was enough for the experiments at 1500°C. In addition, the attainment of equilibrium was also evaluated by approaching the final condition from two directions, that is, by directly heating the sample to the target temperature and then superheating the sample to 200°C higher than the target temperature before cooling down to the target equilibration temperature. The nearly identical results from both scenarios confirmed their equilibrium states.

2.5 **Compositional analysis**

The chemical compositions of the quenched phases were examined by scanning electron microscopy (Mira3; Tescan) equipped with EDS (ThermoFisher Scientific UltraDry) at Aalto University and compared to the EPMA (SX100; Cameca) results of the selected samples. The EPMA analyses were conducted at the Geological Survey of Finland (GTK). Since the glass phase contained Na₂O, the concentration of which might decrease during analysis, the device parameters had to be adjusted to avoid the depletion of Na₂O.^{23,24} During the EDS analyses, the acceleration voltage and beam current were set to 15 kV and 11 nA, respectively. In the EDS composition measurements, area analyses were used instead of spot analyses. The standards employed for EDS analysis were tugtupite, quartz, Ti metal, and olivine for Na, Si, Ti, and O, respectively. For the EPMA measurements, the accelerating voltage and beam current were 20 kV and 20 nA, respectively. A focused or defocused beam (diameter from 5 to 10 µm) was employed depending on the available phase areas. The EPMA results were corrected using the PAP online correction program to handle the Na modification.^{23–25} The natural and synthetic minerals and metals listed in Table 2 were applied as external standards in the EPMA measurement.

Table 3 shows the comparison between the EDS and EPMA analysis results for the liquid (glassy structure) and solid phases formed during the equilibration of sample #325. The EDS analysis was in good agreement with the EPMA measurement for both liquid and solid phases. This means that the EDS method with the standards applied is reliable and can be used for analyzing the quenched phases containing Na₂O, SiO₂, and TiO₂ in the present

Rapid quenched area Preserved and glassy area Altered and crystalized area low cooled area

FIGURE 3 Microstructure of a sample of the Na₂O-TiO₂ system quenched from 1300°C.

Quenching of the sample 2.3

To quench the samples, they were dropped into ice-cold water. Compositions of the phases stable at high temperatures were retained after quenching. The liquid phase was preserved as a glassy phase. Samples that contained low SiO₂ could not be retained as a glassy liquid phase once quenched at 1400°C; instead they formed a microcrystalline structure. Figure 3 shows a sample quenched from 1300°C. The glassy structure only formed around the surface that contacted the icy water first. The liquid phase located beyond $\approx 100 \,\mu m$ from the surface was unavoidably partially crystallized. Therefore, for the experiment on the binary Na₂O-TiO₂ without SiO₂, the well-quenched phase was analyzed only up to 1300°C. However, when SiO2 was added to the mixture, well-quenched phases were obtained up to 1600°C.

Equilibrium confirmation 2.4

Attainment of equilibrium was evaluated by checking the homogeneity of the sample to ensure the absence of concentration gradients in the quenched samples. The glass phase was homogeneous, meaning that the analyzed phase represented the equilibrium composition where all elementary reactions were completed during equilibration and no changes took place during quenching. Variation of equilibration time was also considered for ensuring equilibrium conditions. Experiments were performed at different holding times and at specific temperatures. For



Journal

Journal 6311

TABLE 3 Comparison between the results of Electron Probe Microanalyzer (EPMA) and energy-dispersive X-ray spectroscopy (EDS) measurements for sample #325.

		True stoichiometric							
EPMA (mol%)			EDS (mol%)			composition (mol%)			
Na ₂ O	SiO ₂	TiO ₂	Na ₂ O	SiO ₂	TiO ₂	Na ₂ O	SiO ₂	TiO ₂	Phase
24.30	0	75.40	24.91	0	74.80	25.00	0	75.00	$Na_2Ti_3O_7$
14.12	0	85.83	14.83	0	84.94	14.29	0	85.71	$Na_2Ti_6O_{13}$
28.7	26.9	44.3	30.5	24.7	44.8				Liquid



FIGURE 4 Micrographs of the liquid at saturation with (A) SiO₂, (B) TiO₂, (C) Na₂Ti₃O₇, and (D) Na₂Ti₆O₁₃.

investigation. For the solid phases, the difference between the EDS results and the stoichiometric values was less than 1 mol%. A chemical analysis uncertainty of around 2 mol% was found for the EDS analysis of the liquid phases. For the liquid phase analysis of Na₂O and TiO₂, the difference between EPMA and EDS analysis was less than 2 mol%. In addition, the reliability of the EDS can be evaluated from the result of the solid phases analysis. This is because the theoretical stoichiometric compositions of the solid were known, and measurement of the liquid phases was carried out together with that of the solid phases, and the applied parameters and standards were not changed.

2.6 | Computation of phase diagram

The experimental data obtained in the present investigation were compared with the computed ternary diagrams with MTDATA software, utilizing the HTOX database (earlier MTOX), version 9.1^{26} by Hampton



FIGURE 5 Micrographs of the liquid at saturation with (A) Na_2SiTiO_5 , (B) TiO_2 and $Na_2Ti_6O_{13}$, (C) SiO_2 and TiO_2 , (D) $Na_2Ti_6O_{13}$ and Na_2TiO_5 , (E) Na_2TiO_5 and $Na_2Ti_3O_7$, and (F) $Na_2Ti_3O_7$ and $Na_2Ti_6O_{13}$.

Thermodynamics Ltd. HTOX database for the Na₂O-SiO₂-TiO₂ system was derived based on experimental data available in the literature including the data from Glasser and Marr.¹¹ Liquidus data calculated using FactSage 8.1 and FToxid database²⁷ were also compared with the data

6312

obtained in the present investigation. The model used in the MTOX database²⁶ of MTDATA is an associated species model described in Barry et al.²⁸ and validated in several publications, for example, Taskinen et al.²⁹ and Gisby et al.²⁶

TABLE 4 Phase assemblages and their microstructures obtained in the present study.

#	Phase assemblages	Microstructure figure
1	Liquid + SiO ₂	4A
2	Liquid + TiO_2	4B
3	Liquid + Na ₂ Ti ₃ O ₇	4C
4	Liquid + $Na_2Ti_6O_{13}$	4D
5	Liquid + Na_2TiSiO_5	5A
6	$Liquid + SiO_2 + Na_2Ti_6O_{13}$	5B
7	$Liquid + SiO_2 + TiO_2$	5C
8	$Liquid + Na_2Ti_6O_{13} + Na_2SiTiO_5$	5D
9	$Liquid + Na_2SiTiO_5 + Na_2Ti_3O_7$	5E
10	$Liquid + Na_2Ti_6O_{13} + Na_2Ti_3O_7$	5F

3 | RESULTS AND DISCUSSION

In the present investigation, 10-phase assemblages of liquid phase saturated with one or multiple solid phases were obtained. The phase assemblages were liquid saturated with a single solid phase of SiO_2 (Figure 4A), TiO_2 (Figure 4B), Na₂Ti₃O₇ (Figure 4C), Na₂Ti₆O₁₃ (Figure 4D), Na₂SiTiO₅ (Figure 5A), and a doubly saturated liquid with phases of TiO₂ and Na₂Ti₆O₁₃ (Figure 5B); SiO₂ and TiO₂ (Figure 5C); Na₂Ti₆O₁₃ and Na₂SiTiO₅ (Figure 5D), Na_2SiTiO_5 and $Na_2Ti_3O_7$ (Figure 5E), and $Na_2Ti_6O_{13}$ and Na₂Ti₃O₇ (Figure 5F), as shown in Table 4. The compositional EDS analyses of the quenched samples are shown in Table 5 and their microstructures are presented in Figures 4 and 5. The compositions of liquid in saturation with two solid phases compared with HTOX²⁶ and FToxid²⁷ databases are presented in Table 6. The data and the suggested phase relations obtained in the present investigation are reported as isothermal sections in Figures 6–13, from 900 to 1600°C, respectively, and compared with the results from Glasser and Marr¹¹ and the liquidus line computed using the HTOX database.²⁶ The liquid composition at one solid phase saturation is presented as experimental tie lines in the diagrams, while the liquid composition in equilibrium with two solid phases is presented as the tie triangle. The data are also plotted as liquidus projections in Figure 14.

The present investigation measured the new liquidus composition data at SiO₂ saturation at 1500 and 1600°C. The previous work by Santoso and Taskinen¹² on the Na₂O-SiO₂ binary system was plotted on the graphs and is consistent with the current experimental data, as shown in Figures 6–13. The primary phase field of SiO₂ is wider than that reported by Glasser and Marr¹¹ meaning that liquid at SiO2 saturation can dissolve more TiO₂ than determined by Glasser and Marr.¹¹ It also means that in the present investigation, the univariant line, the intersection of the field of SiO_2 and TiO_2 , is shifted to the TiO_2 apex. The liquidus temperatures for the compositions located close to the univariant line are significantly different from those of Glasser and Marr.¹¹ For example, the mixture with mole fractions of 0.096, 0.676, and 0.228 (sample #82) for Na₂O, SiO_2 , and TiO_2 is fully molten far above 1400°C according to their work.¹¹ In contrast, the mixture of sample #82 is fully molten at temperatures just above 1300°C, based on the data obtained in the present investigation.

At 1000–1200°C, the liquidus composition at SiO₂ saturation and the univariant line where the liquid phase is saturated with two solid phases, SiO₂ and TiO₂, are in good agreement with the prediction of the HTOX database 26 (Table 6). FToxid²⁷ predicts this univariant composition slightly higher and lower in SiO₂ and TiO₂ content in the liquid (Table 6) sample #117. For example, the concentration of SiO₂ and TiO₂ in the mole fraction of sample #117 obtained in the present investigation are 0.65 and 0.212, respectively. According to HTOX²⁶ concentrations of SiO₂ and TiO₂ are 0.656 and 0.216, respectively and FToxid²⁷ predicts the concentration of SiO₂ and TiO₂ are 0.673 and 0.912, respectively. However, at a high temperature of 1500°C, the liquidus at SiO₂ saturation obtained in the present investigation shows lower silica concentrations than the HTOX prediction²⁶ and in good agreement with FToxid prediction.²⁷

The present investigation also determined new liquidus compositions at TiO₂ saturation at 1500 and 1600°C. At TiO₂ saturation, the liquidus line of 1400°C drawn by Glasser and Marr¹¹ could cut the liquidus line of 1200°C obtained by the present investigation. This indicates that the liquidus points of some TiO₂-rich mixtures obtained in the present investigation are 200°C lower than those reported by Glasser and Marr.¹¹ Despite the apparent differences, the data of the present investigation at TiO₂ saturation are in good agreement with the HTOX prediction²⁶ at low and high temperatures, as shown in Figures 7 and 13, respectively. However, FToxid²⁷ computed the liquidus composition at TiO₂ saturation slightly higher in Na₂O concentrations at 1500 and 1600°C.

The liquid composition at double solid saturations of TiO_2 and $Na_2Ti_6O_{13}$, however, displayed a much lower SiO_2 content than the prediction by the $HTOX^{26}$ and $FToxid^{27}$ databases. For example, based on the data obtained in the present investigation, SiO_2 concentration in the liquid phase in equilibrium with TiO_2 and $Na_2Ti_6O_{13}$ phases at 1000°C is 0.458 in mole fraction, whereas the computation by the $HTOX^{26}$ and $FToxid^{27}$ databases are 0.555 and 0.545 respectively (Table 6, sample #144). This means that, in the computed ternary diagram, the univariant line, where the primary phase fields of TiO_2

TABLE 5	Compositions of the liquid phase obtained in the present investigation using energy-dispersive X-ray spectroscopy (EDS).

6314 Journal

	Equilibration	Temperature		Composition (mol fraction)		
Sample #	time (h)	(°C)	Phases	Na ₂ O	SiO ₂	TiO ₂
123	25	900	Liquid	0.309	0.484	0.207
			Na ₂ TiSiO ₅	0.336	0.324	0.340
130	25	900	Liquid	0.225	0.542	0.233
			TiO ₂	-	-	1
			Na ₂ Ti ₆ O ₁₃	0.150	-	0.850
269	45	900	Liquid	0.190	0.670	0.140
			SiO_2	-	1	-
271	45	900	Liquid	0.179	0.636	0.185
			TiO ₂	-	-	1
			SiO_2	-	1	-
272	45	900	Liquid	0.209	0.575	0.216
			TiO ₂	-	_	1
273	45	900	Liquid	0.241	0.518	0.241
			Na ₂ Ti ₆ O ₁₃	0.145	-	0.855
274	45	900	Liquid	0.412	0.310	0.278
			Na ₂ TiSiO ₅	0.342	0.328	0.330
277	45	900	Liquid	0.417	0.337	0.246
			Na ₂ TiSiO ₅	0.342	0.320	0.338
279	45	900	Liquid	0.398	0.187	0.415
			Na ₂ Ti ₃ O ₇	0.250	-	0.750
280	45	900	Liquid	0.193	0.654	0.153
			SiO ₂	-	1	-
281	45	900	Liquid	0.410	0.280	0.310
			Na ₂ TiSiO ₅	0.344	0.324	0.332
282	45	900	Liquid	0.196	0.687	0.117
			SiO ₂	-	1	-
283	45	900	Liquid	0.386	0.241	0.373
			Na ₂ TiSiO ₅	0.343	0.339	0.318
			Na ₂ Ti ₃ O ₇	0.255	-	0.745
287	41	900	Liquid	0.274	0.464	0.262
			$Na_2Ti_6O_{13}$	0.137	-	0.863
288	41	900	Liquid	0.335	0.493	0.172
			Na ₂ TiSiO ₅	0.332	0.319	0.349
290	41	900	Liquid	0.299	0.464	0.237
			Na ₂ TiSiO ₅	0.337	0.327	0.336
291	41	900	Liquid	0.378	0.456	0.166
			Na ₂ TiSiO ₅	0.342	0.332	0.326
292	41	900	Liquid	0.192	0.604	0.204
			TiO ₂	-	-	1
293	41	900	Liquid	0.282	0.436	0.282
			Na ₂ TiSiO ₅	0.332	0.336	0.332
			$Na_2Ti_6O_{13}$	0.139	-	0.861
320	46	900	Liquid	0.194	0.708	0.098
			SiO ₂	-	1	-
					(a

(Continues)

TABLE 5 (Continued)

	Equilibration	Temperature		Composition (mol fraction)		
Sample #	time (h)	(°C)	Phases	Na ₂ O	SiO ₂	TiO ₂
321	46	900	Liquid	0.256	0.493	0.251
			Na ₂ Ti ₆ O ₁₃	0.136	-	0.864
137	37	1000	Liquid	0.338	0.156	0.506
			Na ₂ Ti ₃ O ₇	0.239	-	0.761
138	37	1000	Liquid	0.175	0.733	0.092
			SiO ₂	_	1	-
144	27	1000	Liquid	0.239	0.458	0.303
			Na ₂ Ti ₆ O ₁₃	0.135	-	0.865
			TiO ₂	-	_	1
145	27	1000	Liquid	0.269	0.390	0.341
			Na ₂ Ti ₆ O ₁₃	0.138	_	0.862
146	27	1000	Liquid	0.285	0.331	0.384
			Na ₂ Ti ₆ O ₁₃	0.138	_	0.862
148	24	1000	Liquid	0.157	0.641	0.202
			SiO ₂	_	1	_
			TiO ₂	_	_	1
149	24	1000	Liquid	0.199	0.546	0.255
			TiO	_	_	1
325	24	1000	Liquid	0.304	0.247	0.449
020		1000	Na ₂ Ti ₂ O ₁₂	0.136	_	0.864
			$Na_2 Ti_6 O_{13}$	0.240	_	0.760
328	24	1000	Liquid	0.274	0 367	0.359
520	24	1000	Na-Ti-O	0.138	-	0.862
320	24	1000	Liquid	0.138		0.602
525	24	1000	Na Ti O	0.375	_	0.025
100	1	1100	Liquid	0.233	0.484	0.745
100	-	1100	TiO	0.200	-	1
102	12	1100	Liquid	0.283	0 147	1
105	15	1100		0.285	0.147	0.970
104	12	1100	Liquid	0.137	0.072	0.600
104	15	1100	Na Ti O	0.288	0.075	0.039
105	12	1100	$\operatorname{Ka}_2 \operatorname{H}_6 \operatorname{O}_{13}$	0.130	0 177	0.543
105	15	1100		0.230	0.177	0.945
116	12	1100	Liquid	0.141	- 0.515	0.039
110	15	1100	TiO	0.192	0.515	0.295
117	12	1100	HO ₂	- 0.129	-	1
117	15	1100	Tiquid	0.138	0.049	0.215
			110 ₂	-	-	1
110	12	1100	SIO ₂	-	1	-
119	13	1100	Liquid	0.179	0.770	0.051
101	12	1100	SIO ₂	- 0.194	1	-
121	15	1100	Tiquiu	0.184	0.540	0.276
122	12	1100	IIO ₂	-	0 717	1
122	15	1100	Liquid	0.146	0.717	0.137
			S10 ₂	-	1	-

(Continues)

TABLE 5 (Continued)

15512916, 2024.9, Downloaded from https://ceramics.onlinefibrary.wiley.com/doi/10.1111/jace.19845 by Aalto University, Wiley Online Library on [04/07/2024]. See the Terms and Conditions (https://onlinefibrary.wiley.com/terms

	Equilibration	Temperature		Composition (mol fraction)			
Sample #	time (h)	(°C)	Phases	Na ₂ O	SiO ₂	TiO ₂	
198	16	1100	Liquid	0.234	0.356	0.410	
			Na ₂ Ti ₆ O ₁₃	0.134	-	0.866	
			TiO ₂	-	-	1	
201	16	1100	Liquid	0.227	0.389	0.384	
			TiO ₂	-	-	1	
202	16	1100	Liquid	0.257	0.294	0.449	
			Na ₂ Ti ₆ O ₁₃	0.135	-	0.865	
206	22	1100	Liquid	0.277	0.208	0.515	
			$Na_2Ti_6O_{13}$	0.135	-	0.865	
352	15	1100	Liquid	0.334	-	0.666	
			Na ₂ Ti ₃ O ₇	0.245	-	0.755	
36	5	1200	Liquid	0.265	0.049	0.686	
			Na ₂ Ti ₆ O ₁₃	0.135	-	0.865	
37	5	1200	Liquid	0.242	0.146	0.612	
			Na ₂ Ti ₆ O ₁₃	0.133	-	0.867	
39	6	1200	Liquid	0.243	0.188	0.569	
			Na ₂ Ti ₆ O ₁₃	0.139	-	0.861	
			TiO ₂	-	-	1	
41	6	1200	Liquid	0.112	0.665	0.223	
			SiO ₂	_	1	-	
			TiO ₂	_	_	1.000	
52	6	1200	Liquid	0.133	0.711	0.156	
			SiO ₂	-	1	-	
53	6	1200	Liquid	0.138	0.732	0.130	
			SiO ₂	_	1	-	
210	22	1200	Liquid	0.178	0.488	0.334	
			TiO ₂	-	-	1	
212	22	1200	Liquid	0.157	0.760	0.083	
			SiO ₂	-	1	-	
213	22	1200	Liquid	0.136	0.614	0.250	
			TiO ₂	-	-	1	
214	22	1200	Liquid	0.155	0.565	0.280	
			TiO ₂	_	_	1	
215	22	1200	Liquid	0.198	0.408	0.394	
			TiO ₂	-	-	1	
216	22	1200	Liquid	0.221	0.323	0.456	
			TiO_2	_	_	1	
218	22	1200	Liquid	0.230	0.226	0.544	
			TiO ₂	-	-	1	
220	22	1200	Liquid	0.225	0.271	0.504	
			TiO ₂	_	-	1	
263	18	1200	Liquid	0.258	-	0.742	
			Na ₂ Ti ₆ O ₁₃	0.135	-	0.865	

-and-conditions) on Wiley Online Library for rules of use; OA articles are governed by the applicable Creative Commons License

TABLE 5 (Continued)

	Equilibration	Temperature		Composition (mol fraction)		
Sample #	time (h)	(°C)	Phases	Na ₂ O	SiO ₂	TiO ₂
53-a	6	1200	Liquid	0.144	0.747	0.109
			SiO ₂	_	1	-
66	4	1300	Liquid	0.209	0.186	0.605
			TiO ₂	-	-	1
69	4	1300	Liquid	0.203	0.284	0.513
			TiO ₂	-	-	1
71	4	1300	Liquid	0.203	0.319	0.478
			TiO ₂	-	-	1
79	14	1300	Liquid	0.141	0.539	0.320
			TiO ₂	-	-	1
80	14	1300	Liquid	0.133	0.563	0.304
			TiO ₂	-	-	1
82	14	1300	Liquid	0.096	0.676	0.228
			SiO_2	-	1	-
			TiO ₂	-	-	1
86	11	1300	Liquid	0.121	0.592	0.287
			TiO ₂	-	-	1
95	15	1300	Liquid	0.113	0.623	0.264
			TiO ₂	-	-	1
96	15	1300	Liquid	0.167	0.447	0.386
			TiO ₂	-	-	1
99	4	1300	Liquid	0.157	0.481	0.362
			TiO ₂	_	-	1
223	6	1300	Liquid	0.215	0.112	0.673
			TiO ₂	-	-	1
224	6	1300	Liquid	0.128	0.796	0.076
			SiO ₂	_	1	-
250	6	1300	Liquid	0.201	-	0.799
			TiO ₂	-	-	1
162	4	1400	Liquid	0.186	0.150	0.664
			TiO ₂	-	_	1
166	4	1400	Liquid	0.175	0.294	0.531
			TiO ₂	-	-	1
168	4	1400	Liquid	0.063	0.735	0.202
			SiO ₂	-	1	-
			TiO ₂	-	_	1
170	4	1400	Liquid	0.112	0.823	0.065
			SiO ₂	-	1	-
311	6	1400	Liquid	0.130	0.502	0.368
			TiO ₂	-	-	1
312	6	1400	Liquid	0.125	0.517	0.358
			TiO ₂	-	-	1

(Continues)

6318 JOURNAL

TABLE 5 (Continued)

SampleInice (b)(C)PhasesNa,00Sio,100,313-140010,010.1430.600.31314-140010,010.0740.520.323156140014quid0.1160.5230.3270,110,010.4010.4021356140014quid0.0120.8030.1081447150014quid0.0170.8840.071767100100,01-111777100100,010.0210.0210.0211787150014quid0.0210.680.222170,7150014quid0.0210.680.22118014quid0.0210.680.22210,011018014quid0.0210.680.22210,011018014quid0.0210.680.22110,011019014quid0.0210.6910,01101019014quid0.0210.6910,011010191190014quid0.0100.14144210191190114quid0.1500.1410101911901190119010.160.14101911901190119010.101010191190119010.10<		Equilibration	tion Temperature		Composition (mol fraction)		
313 6 100 101 0.13 0.13 0.13 0.13 0.13 0.13 0.13 314 6 100 100 0.04 0.90 0.20 315 6 100 100 0.16 0.20 0.20 315 6 100 100 0.16 0.20 0.20 170 7 100 100 0.40 0.40 0.40 170 7 100 100 0.40 0.40 0.40 171 7 100 100 0.40 0.40 0.40 172 7 100 100 0.40 0.40 0.40 173 7 100 100 0.7 0.00 0.7 174 7 100 100 0.7 0.00 0.7 174 7 100 100 0.7 0.00 0.00 174 7 100 100 0.00 0.00 0.00 174 100 100 100 0.00 0.00 0.00 174 100 100 0.01 0.7 0.00 0.00 174 100 100 100 <td< td=""><td>Sample #</td><td>time (h)</td><td>(°C)</td><td>Phases</td><td>Na₂O</td><td>SiO₂</td><td>TiO₂</td></td<>	Sample #	time (h)	(°C)	Phases	Na ₂ O	SiO ₂	TiO ₂
Pick Pick <th< td=""><td>313</td><td>6</td><td>1400</td><td>Liquid</td><td>0.143</td><td>0.466</td><td>0.391</td></th<>	313	6	1400	Liquid	0.143	0.466	0.391
314 6 1400 14pid input field 0.074 0.969 0.208 170 - - 1 170 - - 0.032 0.032 174 6 1400 14qiud 0.042 0.032 0.032 174 7 1500 14quid 0.042 0.486 0.475 175 7 1500 14quid 0.072 0.486 0.475 176 7 1500 14quid 0.072 0.486 0.475 177 7 1500 14quid 0.074 0.486 0.405 178 7 1500 14quid 0.074 0.486 0.405 179 7 1500 14quid 0.074 0.486 0.402 179 7 1500 14quid 0.074 0.486 0.402 180 7 1500 14quid 0.166 0.432 0.422 181 7 1500 14quid 0.166 0.424 0.424 190 190 170 - 1 1 244 7 1500 14quid 0.314 0.424 1 190 190				TiO ₂	-	_	1
TiO213151400161pd0.1160.1160.16211747150014pdd0.0420.800.0081767150014pdd0.0420.800.4071767150014pdd0.0740.8680.4071777150014pdd0.0740.8680.4071787150014pdd0.0720.6360.2021787150014pdd0.0720.6360.2021797150014pdd0.0720.6360.2021707150014pdd0.1300.4740.3141807150014pdd0.1300.4740.31419014pdd0.1300.4020.4020.4020.402190150014pdd0.1600.4020.4020.402191150014pdd0.1600.4020.4020.402191150014pdd0.1600.4020.4020.4021927150014pdd0.1610.4020.40219319014pdd0.0310.4020.4020.40219419014pdd0.0310.4030.4040.3010.40319419014pdd0.0310.4030.4040.3010.40419419014pdd0.0310.4040.3010.4040.3010.404 </td <td>314</td> <td>6</td> <td>1400</td> <td>Liquid</td> <td>0.074</td> <td>0.696</td> <td>0.230</td>	314	6	1400	Liquid	0.074	0.696	0.230
13. 6 1400 14µµµµµµµµµµµµµµµµµµµµµµµµµµµµµµµµµµµµ				TiO ₂	-	_	1
Independent of the set of t	315	6	1400	Liquid	0.116	0.552	0.332
174 7 1500 Liquid SiO ₂ 0.042 0.850 0.108 SiO ₂ 176 7 1500 1quid 0.070 0.486 0.487 177 7 1500 1quid 0.074 0.486 0.058 177 7 1500 1quid 0.074 0.868 0.058 178 7 1500 1quid 0.072 0.636 0.292 170 7 1500 1quid 0.072 0.636 0.292 170 7 1500 1quid 0.072 0.636 0.292 180 7 1500 1quid 0.010 0.347 0.533 170 7 1500 1quid 0.105 0.442 0.422 240 7 1500 1quid 0.105 0.519 0.376 170 7 1500 1quid 0.105 0.519 0.376 170 7 1500 1quid 0.016 0.519 0.376 170 7 1500 1quid 0.016 0.519 0.376 171 1500 1quid 0.016 0.51 0.519 0.376 184 1 1600<				TiO ₂	-	_	1
NO-1-1767150014quid 1000.1070.4860.4071707150016quid 1000.0740.8880.0281787150016quid 1000.0720.6360.2921787150016quid 1000.0660.8880.0781807150016quid 1000.0660.8880.0781807150016quid 1000.0660.8880.0781817150016quid 	174	7	1500	Liquid	0.042	0.850	0.108
176 7 1500 Liquid 0.107 0.486 0.407 177 7 1500 Liquid 0.074 0.888 0.292 178 7 1500 Liquid 0.074 0.636 0.292 178 7 1500 Liquid 0.074 0.636 0.292 180 7 1500 Liquid 0.066 0.88 0.292 180 7 1500 Liquid 0.066 0.83 0.292 181 7 1500 Liquid 0.066 0.83 0.292 181 7 1500 Liquid 0.105 0.347 0.533 170 7 1500 Liquid 0.106 0.442 0.442 1240 7 1500 Liquid 0.106 0.519 0.376 1241 7 1500 Liquid 0.106 0.519 0.106 1242 7 1500 Liquid 0.106 0.519 0.106 1243 7 1500 Liquid 0.106 0.519 0.106 1244 7 1500 Liquid 0.107 0.414 1.16 1247 1 1600 <td></td> <td></td> <td></td> <td>SiO₂</td> <td>-</td> <td>1</td> <td>_</td>				SiO ₂	-	1	_
102 - - 1 177 7 1500 16µid 0.074 0.868 0.058 180 7 1500 16µid 0.072 0.636 0.292 170 7 1500 16µid 0.072 0.636 0.292 180 7 1500 16µid 0.072 0.636 0.393 181 7 1500 16µid 0.105 0.347 0.533 190 16µid 0.101 0.41 0.434 0.434 240 7 1500 16µid 0.105 0.519 0.376 170_ 7 1500 16µid 0.105 0.519 0.376 170_ 7 1500 16µid 0.105 0.519 0.376 170_ 7 1500 16µid 0.105 0.519 0.376 184 1 1600 16µid 0.057 0.4 1 184 1 1600<	176	7	1500	Liquid	0.107	0.486	0.407
$\begin{array}{cccccccccccccccccccccccccccccccccccc$				TiO ₂	_	_	1
$\begin{array}{ c c c c } & c c c c$	177	7	1500	Liquid	0.074	0.868	0.058
$\begin{array}{ c c c c c } 180 & 160 & 160 & 160 & 0.282 & 0.686 & 0.292 & 160 & 170 & - & - & 1 & 170 & 170 & 170 & - & - & 170 & 170 & - & - & - & 170 & - & - & - & 170 & - & - & - & - & - & - & - & - & - & $				SiO	_	1	_
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	178	7	1500	Liquid	0.072	0.636	0 292
180 7 1500 16quid SiO2 - 1 181 7 1500 Liquid 0.130 0.347 0.523 160 7 1500 Liquid 0.100 0.442 0.442 240 7 1500 Liquid 0.105 0.519 0.376 1702 - - 1 1 1 1 1 243 7 1500 Liquid 0.105 0.519 0.376 1702 - - 1	170	,	1500	TiQ.	_	-	1
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	190	7	1500	Liquid	0.066	0.959	0.076
181 7 1500 Liquid 0.10 0.347 0.523 1702 - - - 1 240 7 1500 Liquid 0.116 0.442 0.442 7 1500 Liquid 0.116 0.442 0.442 7 1500 Liquid 0.015 0.519 0.76 7 1500 Liquid 0.031 0.795 0.174 18 11 1600 Liquid 0.057 0.594 0.349 190 11 1600 Liquid 0.091 0.404 0.55 191 1600 Liquid 0.052 0.609 0.339 191 1600 Liquid 0.052 0.609 0.339 <	100	1	1500	SiO	0.000	1	0.070
IAI I AU IAU IAU <thiau< td="" th<=""><td>101</td><td>7</td><td>1500</td><td>SIO₂</td><td>-</td><td>1</td><td>-</td></thiau<>	101	7	1500	SIO ₂	-	1	-
140 7 1500 1602 7 1604 6042 0.442 0.442 0.442 243 7 1500 Liquid 0.105 0.519 0.376 244 7 1500 Liquid 0.031 0.795 0.174 244 7 1500 Liquid 0.031 0.795 0.174 247 7 1500 Liquid 0.050 0.165 0.685 102 - - - 1 1600 1002 - 0.016 0.434 188 11 1600 Liquid 0.091 0.404 0.505 1702 - - 1 <td>181</td> <td>1</td> <td>1500</td> <td>Liquid</td> <td>0.130</td> <td>0.347</td> <td>0.525</td>	181	1	1500	Liquid	0.130	0.347	0.525
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		-		110 ₂	-	-	1
Participant and provide and pro	240	7	1500	Liquid	0.116	0.442	0.442
243 7 1500 Liquid 0.105 0.519 0.376 TiO2 - - 1 244 7 1500 Liquid 0.010 0.795 0.174 70 1500 Liquid 0.150 0.165 0.685 TiO2 - - 1 0.594 0.349 18 11 1600 Liquid 0.057 0.594 0.349 18 11 1600 Liquid 0.057 0.594 0.349 190 11 1600 Liquid 0.057 0.594 0.369 190 11 1600 Liquid 0.039 0.693 0.268 190 11 1600 Liquid 0.039 0.693 0.268 191 192 11 1600 Liquid 0.052 0.609 0.339 192 11 1600 Liquid 0.030 0.411 102 193 11				TiO ₂	-	-	1
TiO2 - - - 1 244 7 1500 Liquid 0.031 0.795 0.74 102 - - 1 102 - 1 247 1500 Liquid 0.031 0.795 0.685 138 1 1600 Liquid 0.057 0.594 0.349 189 1 1600 Liquid 0.091 0.404 0.505 1702 - - - 1	243	7	1500	Liquid	0.105	0.519	0.376
244 7 1500 Liquid 0.031 0.795 0.744 70 1500 TiO2 - - 1 247 7 1500 Liquid 0.150 0.165 0.685 TiO2 - - 1 1 188 1 1600 Liquid 0.097 0.594 0.494 189 11 1600 TiO2 - - 1 189 11 1600 Liquid 0.091 0.693 0.268 190 11 1600 Liquid 0.091 0.693 0.268 191 11 1600 Liquid 0.092 0.693 0.268 192 11 1600 Liquid 0.052 0.609 0.339 192 11 1600 Liquid 0.052 0.609 0.339 193 11 1600 Liquid 0.035 0.711 0.254 193 11 1600 Liquid 0.030 0.747 0.223 193 11 1600 TiO2 - - 1 194 1600 Liquid 0.036 0.747 0.233 195				TiO ₂	-	-	1
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	244	7	1500	Liquid	0.031	0.795	0.174
247 7 1500 Liquid 0.150 0.165 0.685 TiO2 - - 1 188 1 1600 Liquid 0.057 0.594 0.349 189 1 1600 Liquid 0.091 0.404 0.505 190 1 1600 Liquid 0.091 0.404 0.508 190 1 1600 Liquid 0.091 0.404 0.508 190 1 1600 Liquid 0.039 0.693 0.268 191 1 1600 Liquid 0.052 0.609 0.339 192 1 1600 Liquid 0.035 0.101 0.441 193 1 1600 Liquid 0.035 0.411 0.411 193 1 1600 Liquid 0.030 0.427 0.431 194 1600 Liquid 0.036 0.427 0.437 195 <td< td=""><td></td><td></td><td></td><td>TiO₂</td><td>-</td><td>-</td><td>1</td></td<>				TiO ₂	-	-	1
ID2 - - 1 188 1 1600 Liquid 0.057 0.594 0.349 189 1 1600 Liquid 0.091 0.404 0.505 190 1 1600 Liquid 0.091 0.404 0.505 102 - - - 1 1 190 1 1600 Liquid 0.039 0.693 0.268 191 1600 Liquid 0.052 0.609 0.339 192 1 1600 Liquid 0.052 0.609 0.339 192 1 1600 Liquid 0.035 0.71 1 193 1 1600 Liquid 0.035 0.411 1 193 1 1600 Liquid 0.030 0.412 1 194 1600 Liquid 0.030 0.417 1 195 1 Liquid 0.086 0.427 <td>247</td> <td>7</td> <td>1500</td> <td>Liquid</td> <td>0.150</td> <td>0.165</td> <td>0.685</td>	247	7	1500	Liquid	0.150	0.165	0.685
188 11 1600 Liquid 0.057 0.594 0.349 TiO2 - - 1 189 11 1600 Liquid 0.091 0.404 0.505 TiO2 - - 1 <td></td> <td></td> <td></td> <td>TiO₂</td> <td>-</td> <td>-</td> <td>1</td>				TiO ₂	-	-	1
$\begin{array}{ c c c c c c } & \ & \ & \ & \ & \ & \ & \ & \ & \ & $	188	11	1600	Liquid	0.057	0.594	0.349
189 11 1600 Liquid 0.091 0.404 0.505 TO2 - - 1 190 11 1600 Liquid 0.039 0.693 0.268 190 19 - - - 1 191 1600 Liquid 0.052 6.609 0.339 192 19 1600 Liquid 0.035 0.711 0.268 192 19 1600 Liquid 0.035 0.711 0.268 193 19 1600 Liquid 0.035 0.711 0.268 193 19 1600 Liquid 0.030 0.481 0.446 195 11 1600 Liquid 0.030 0.747 0.223 194 1600 Liquid 0.036 0.427 0.481 194 1600 Liquid 0.866 0.427 0.481 195 14 1600 Liquid 1 </td <td></td> <td></td> <td></td> <td>TiO₂</td> <td>-</td> <td>-</td> <td>1</td>				TiO ₂	-	-	1
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	189	11	1600	Liquid	0.091	0.404	0.505
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$				TiO ₂	_	_	1
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	190	11	1600	Liquid	0.039	0.693	0.268
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$				TiO ₂	-	_	1
${egin{array}{cccccccccccccccccccccccccccccccccccc$	191	11	1600	Liquid	0.052	0.609	0.339
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$				TiO	_	_	1
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	192	11	1600	Liquid	0.035	0.711	0.254
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$			1000	TiO	_	_	1
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	193	11	1600	Liquid	0.073	0 481	0 446
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	1)5	11	1000	TiO	-	-	1
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	105	11	1600	Liquid	- 0.020	0 747	0 222
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	195	11	1000	TiQ	0.050	0.747	1
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	20.4	14	1600	Liquid	-	-	1
1102 - - 1 295 14 1600 Liquid - 0.947 0.053 SiO2 - 1 - 297 14 1600 Liquid - 0.833 0.167 TiO2 - - 1 - 1 1	294	14	1000	Liquia	0.086	0.427	0.487
$\begin{array}{cccccccccccccccccccccccccccccccccccc$				1102	-	-	1
SiO2 - 1 - 297 14 1600 Liquid - 0.833 0.167 TiO2 - - 1 - 1 -	295	14	1600	Liquid	-	0.947	0.053
297 14 1600 Liquid - 0.833 0.167 TiO2 - - 1				SiO ₂	-	1	-
TiO ₂ – – 1	297	14	1600	Liquid	-	0.833	0.167
				TiO ₂	-	-	1

TABLE 6 Composition of liquid saturated with two solids phases obtained in the present study compared with $HTOX^{26}$ and $FToxid^{27}$ databases.

			Liquid com with two so	position satur lids	ated	
Sample #	Temperature °C	Origin	Na ₂ O	SiO ₂	TiO ₂	Solid Phases
283	900	Present Study	0.386	0.241	0.373	Na_2SiTiO_5 and $Na_2Ti_3O_7$
		HTOX	0.351	0.200	0.449	
		FToxid	0.397	0.174	0.429	
293	900	Present Study	0.282	0.436	0.282	Na_2SiTiO_5 and $Na_2Ti_6O_{13}$
		HTOX	0.296	0.482	0.222	
		FToxid	n.a.	n.a.	n.a.	
144	1000	Present Study	0.239	0.458	0.303	$\mathrm{Na_2Ti_6O_{13}}$ and $\mathrm{TiO_2}$
		HTOX	0.213	0.555	0.232	
		FToxid	0.209	0.545	0.246	
148	1000	Present Study	0.157	0.641	0.202	SiO_2 and TiO_2
		HTOX	0.157	0.648	0.195	
		FToxid	0.15	0.667	0.183	
325	1000	Present Study	0.304	0.247	0.449	$\mathrm{Na_2Ti_6O_{13}}$ and $\mathrm{Na_2Ti_3O_7}$
		HTOX	0.315	0.154	0.531	
		FToxid	0.312	0.333	0.355	
117	1100	Present Study	0.138	0.649	0.213	SiO ₂ and TiO ₂
		HTOX	0.128	0.656	0.216	
		FToxid	0.135	0.673	0.192	
198	1100	Present Study	0.234	0.356	0.410	$\mathrm{Na_2Ti_6O_{13}}$ and $\mathrm{TiO_2}$
		HTOX	0.243	0.382	0.375	
		FToxid	0.22	0.474	0.306	
39	1200	Present Study	0.243	0.188	0.569	$Na_2Ti_6O1_3$ and TiO_2
		HTOX	0.245	0.147	0.608	
		FToxid	0.221	0.401	0.378	
41	1200	Present Study	0.112	0.665	0.223	${\rm SiO}_2$ and ${\rm TiO}_2$
		HTOX	0.099	0.679	0.222	
		FToxid	0.117	0.685	0.198	
82	1300	Present Study	0.096	0.676	0.228	SiO ₂ and TiO ₂
		HTOX	0.073	0.711	0.216	
		FToxid	0.096	0.704	0.2	
168	1400	Present Study	0.063	0.735	0.202	SiO ₂ and TiO ₂
		HTOX	0.047	0.772	0.181	
		FToxid	0.068	0.748	0.184	

and $Na_2Ti_6O_{13}$ are joined, is higher than that obtained experimentally in the present investigation.

Figure 14 shows that the compound of $Na_2Ti_6O_{13}$ is located inside the TiO₂ primary phase field instead of having its own primary phase field; indicating that $Na_2Ti_6O_{13}$ melts incongruently. The liquidus composition at $Na_2Ti_6O_{13}$ saturation is in good agreement with the HTOX database²⁶ at 1100°C and 1200°C, which is evident in Figures 8 and 9. In the present investigation, liquids in double saturation of $Na_2Ti_6O_{13}$ and Na_2SiTiO_5 were obtained with the concentration of Na_2O , SiO₂, and TiO₂ in mole fraction at 900°C is 0.282; 0.436 and 0.282, respectively, and HTOX²⁶ predict the concentrations of Na₂O, SiO₂, and TiO₂ in mole fraction at 900°C is 0.296; 0.482 and 0.222, respectively (Table 6, sample #293). However, according to FToxid²⁷ computation, the phase relation of liquid with Na₂Ti₆O₁₃ and Na₂SiTiO₅ is not available at 900°C. and data from Glasser and Marr.¹¹ showed that the SiO₂ in the liquid is around 0.5 mole fraction. As the compound of Na₂Ti₃O₇ is situated within the primary phase field of Na₂Ti₆O₁₃, as shown in Figure 14, Na₂Ti₃O₇ melts incongruently as well. Its phase field also

Journal

6319



FIGURE 6 Isothermal section of the Na₂O-SiO₂-TiO₂ system at 900°C.



FIGURE 7 Isothermal section of the Na₂O-SiO₂-TiO₂ system at 1000° C.



FIGURE 8 Isothermal section of the Na₂O-SiO₂-TiO₂ system at 1100°C.



FIGURE 9 Isothermal section of the Na_2O -SiO₂-TiO₂ system at 1200°C.



FIGURE 10 Isothermal section of the $Na_2O-SiO_2-TiO_2$ system at 1300°C.



FIGURE 11 Isothermal section of the $Na_2O-SiO_2-TiO_2$ system at 1400°C.



FIGURE 12 Isothermal section of the Na_2O-SiO_2 -TiO₂ system at 1500°C.



FIGURE 13 Isothermal section of the $Na_2O-SiO_2-TiO_2$ system at 1600°C.

intersects the primary phase field of Na₂SiTiO₅, which appears to be different in terms of shape, that is, circular form, compared to other primary phase fields in the present investigation. This peculiar form agrees with the report by Glasser and Marr.¹¹ According to their research,¹¹ Na₂SiTiO₅ melts congruently at 965°C, meaning that its primary phase field would cease to exist at 1000°C, which agrees with the present work. Based on the present investigation, ternary liquidus can be obtained in the solid phase saturation of SiO₂, TiO₂, Na₂SiTiO₅, Na₂Ti₆O₁₃, Na₂Ti₃O₇, and Na₂SiTiO₅ at 900°C (Figure 6), all the ternary invariant reactions involving the disappearance of their respective phase fields occur below 900°C.



FIGURE 14 Liquidus projection of the $Na_2O-SiO_2-TiO_2$ system obtained from the present investigation between 900 and 1600°C.

4 | CONCLUSIONS

The phase equilibria of the Na₂O-SiO₂-TiO₂ system were investigated at temperatures between 900 and 1600°C in air. Novel liquidus measurements at TiO₂ saturation at 1500 and 1600°C were obtained. The present investigation reported 10 phase assemblages for the liquid at solid saturation with SiO₂, TiO₂, Na₂Ti₆O₁₃, Na₂SiTiO₅, Na₂Ti₃O₇, and in double solid saturation of SiO₂ + TiO₂, TiO₂ + Na₂Ti₆O₁₃, Na₂Ti₆O₁₃ + Na₂Ti₃O₇, Na₂Ti₆O₁₃ + Na₂SiTiO₅, and Na₂SiTiO₅ + Na₂Ti₃O₇. Comparisons with the phase diagram assessed using the HTOX and FToxid databases were carried out between 1000 and 1600°C. Data obtained in the present investigation can be employed to revise and re-optimize the existing phase diagrams and databases containing silica, soda, and titania to obtain a more optimal model.

ACKNOWLEDGMENTS

The authors acknowledge the funding from "Riset Peningkatan Kapasitas Dosen Muda", Institut Teknologi Bandung (ITB). The authors also acknowledge the supplementary funding at Aalto University from Business Finland and the Academy of Finland (project PhosPath #341404). We are highly indebted to Hampton Thermodynamics Ltd (UK) and the members of its industrial support group (project #HTL 001) for access to the recent version of the HTOX oxide database (version 9.1). The Academy of Finland's RawMatTERS Finland Infrastructure (RAMI) based at Aalto University, VTT Technical Research Centre, and the Geological Survey of Finland, was utilized in this research. Preliminary experiments conducted by Mr. Lanjar Grahita at ITB Pyrometallurgy Laboratory are

6322 Journal

also gratefully acknowledged as well as the assistance of the Geological Survey of Finland and Radoslaw Michallik, PhD, for the EPMA verification measurements.

ORCID

Imam Santoso D https://orcid.org/0000-0001-7728-7247 Dmitry Sukhomlinov D https://orcid.org/0000-0002-8752-4776

Min Chen https://orcid.org/0000-0003-0544-4359 Pekka Taskinen https://orcid.org/0000-0002-4054-952X

REFERENCES

- 1. El-Rehim AF, Wahab EA, Halaka MM, Shaaban KH. Optical properties of SiO₂-TiO₂-La₂O₃-Na₂O-Y₂O₃ glasses and a novel process of preparing the parent glass-ceramics. Silicon. 2022;14(2):373-84.
- 2. Sahu P, Ali SM. Tuning network connectivity of silicate and sodium borosilicate glasses by TiO_2 for enhanced chemical durability: molecular dynamics simulation investigations. Langmuir. 2022;38:7639–63.
- Limbach R, Karlsson S, Scannell G, Mathew R, Edén M, Wondraczek L. The effect of TiO₂ on the structure of Na₂O-CaO-SiO₂ glasses and its implications for thermal and mechanical properties. J Non-Cryst Solids. 2017;471:6–18.
- Barton I, Matejec V, Mrazek J, Predoana L, Zaharescu M. Optical properties of Na₂O-TiO₂-SiO₂ glass films prepared by the sol-gel method. Photon Dev Syst VII. 2017;10603:170–76
- 5. Chen LM, Zhen YL, Zhang GH, Wang L, Chen D, Zhao H, et al. Role of Na_2O and TiO_2 on viscosity and structure of Sodium-Titanium-bearing slag. J Non-Cryst Solids. 2023;602:122080.
- Li P, Wang K, Fang M, Zhang L, Jiang D, Li J, et al. Boron removal from silicon by slag refining using Na₂O-SiO₂ in industrial applications. Sep Sci Technol. 2018;53(13):2144–49.
- Kim DH, Heo JH, Park HS, Kim JK, Park JH. Improving the production efficiency of high-titania slag in Ti extraction process: fluxing effect on formation of pseudobrookite. Sci Rep. 2020;10(1):1–12.
- 8. Zulhan Z, Dinillah R, Yulianton T, Santoso I, Hidayat T. Carbothermic reduction of ilmenite concentrate with sodium carbonate additive to produce iron granules and high titania containing slag. Metals. 2022;12(6):963.
- 9. Zhang YM, Yi LY, Wang LN, Chen DS, Wang WJ, Liu YH, et al. A novel process for the recovery of iron, titanium, and vanadium from vanadium-bearing titanomagnetite: sodium modification-direct reduction coupled process. Int J Miner Metall. 2017;24(5):504–11.
- Zhang YM, Wang LN, Chen DS, Wang WJ, Liu Y, Zhao HX, et al. A method for recovery of iron, titanium, and vanadium from vanadium-bearing titanomagnetite. Int J Miner Metall. 2018;25(2):131–44.
- 11. Glasser FP, Marr J. Phase relations in the system Na $_2$ O-TiO $_2$ -SiO $_2$. J Am Ceram. 1979;62(1-2):42–47.
- 12. Santoso I, Taskinen P. Phase equilibria of the Na₂O–SiO₂ system between 1173 and 1873 K. Can Metall Q. 2016;55(2):243–50.
- Santoso I, Riihimäki M, Sibarani D, Taskinen P, Hupa L, Paek MK, et al. Impact of recently discovered sodium calcium silicate solutions on the phase diagrams of relevance for glass-ceramics in the Na₂O-CaO-SiO₂ system. J Eur Ceram. 2022;42(5):2449–63.

 Santoso I, Taskinen P, Jokilaakso A, Paek MK, Lindberg D. Phase equilibria and liquid phase behavior of the K₂O-CaO-SiO₂ system for entrained flow biomass gasification. Fuel. 2020;265:116894.

SANTOSO ET AL.

- Hamilton EH, Cleek GW. Properties of sodium titanium silicate glasses. J Res Nat Bur Std. 1958;61:89–94.
- Vanis M, Zemann J, Pach L. Meranie teploty likvidus a nepriama identifikacia krystalickych faz vysokoteplotnym mikroskopom. Zb Pr Chemickotechnol Fak SVST. 1978;237–42.
- Kirschen M, DeCapitani C, Millot F, Rifflet JC, Coutures JP. Immiscible silicate liquids in the system SiO₂-TiO₂-Al₂O₃. Eur J Mineral. 1999, 11:427–40.
- Kirillova SA, Almjashev VI, Gusarov VV. Phase relationships in the SiO₂-TiO₂ system. Russ J Inorg Chem. 2011;56(9):1464– 71.
- Eriksson G, Pelton AD. Critical evaluation and optimization of the thermodynamic properties and phase diagrams of the MnO-TiO₂, MgO-TiO₂, FeO-TiO₂, Ti₂O₃-TiO₂, Na₂O-TiO₂, and K₂O-TiO₂ systems. Metall Mater Trans B. 1993;24(5):795–805.
- Wu P, Eriksson G, Pelton AD. Optimization of the thermodynamic properties and phase diagrams of the Na₂O–SiO₂ and K₂O–SiO₂ systems. J Am Ceram. 1993;76(8):2059–64.
- Kang YB, Jung IH, Lee HG. Critical thermodynamic evaluation and optimization of the MnO-SiO₂-"TiO₂"-"Ti₂O₃" System. Calphad. 2006;30(3):226–34.
- 22. D'yachkov VI. Features of oxidation of titanium group metals in air. Russ J Appl Chem. 2004;77:1397–403.
- Siivola J. On the evaporation of some alkali metals during the electron microprobe analyses. Geol Soc Finland Bull. 1969;41:85– 91.
- Morgan GB, London D. Effect of current density on the electron microprobe analysis of alkali aluminosilicate glasses. Am Min. 2005;90(7):1131–38.
- Pouchou JL, Pichoir F. Basic expression of "PAP" computation for quantitative EPMA. in: Proceeding of 11th International Congress on X-ray Optics and Microanalysis (ICXOM). Ontario, Canada: Publ Univ Western Ontario; 1986. pp. 249–53.
- Gisby J, Taskinen P, Pihlasalo J, Li Z, Tyrer M, Pearce J, et al. MTDATA and the prediction of phase equilibria in oxide systems: 30 years of industrial collaboration. Metall Mater Trans B. 2017;48(1):91–98.
- 27. Bale CW, Belisle E, Chartrand P, Decterov SA, Eriksson G, Hack K, et al. FactSage thermochemical software and databases—recent developments. Chalpad. 2009;33(2):295–311.
- Barry T, Dinsdale A, Gisby J. Predictive thermochemistry and phase equilibria of slags. JOM. 1993;45(4):32–38.
- Taskinen P, Dinsdale A, Gisby J. Industrial slag chemistry: a case study of computational thermodynamics. Scand J Metall. 2005;34(2):100–107.

How to cite this article: Santoso I, Sibarani D, Hidayat T, Zulhan Z, Sukhomlinov D, Chen M, et al. Phase equilibria of the Na₂O-TiO₂-SiO₂ system between 900 and 1600°C in air. J Am Ceram Soc. 2024;107:6307–22. https://doi.org/10.1111/jace.19845