

Thermodynamic Analysis of Pseudobinary Subsystems of the System CaO—TiO₂—SiO₂

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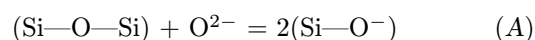
The thermodynamic model taking into account the structural behaviour of TiO₂ in silicate melts was applied to describe the activities of the components in the melts and to calculate the phase diagrams of the systems CaSiO₃—CaTiSiO₅, CaSiO₃—CaTiO₃, Ca₂SiO₄—CaTiO₃, CaTiSiO₅—CaTiO₃, and CaTiSiO₅—TiO₂. When the present TiO₂ is assumed to be completely integrated in the structural network in the form of tetrahedrally coordinated units, *i.e.* it acts as network former, the considered thermodynamic model fits quite well both experimental liquidus curves in the systems CaSiO₃—CaTiSiO₅ and CaTiSiO₅—CaTiO₃ and the CaTiSiO₅ liquidus curve in the system CaTiSiO₅—TiO₂. The model fails in the systems Ca₂SiO₄—CaTiO₃ and CaSiO₃—CaTiO₃ as well as by the TiO₂ liquidus curve in the system CaTiSiO₅—TiO₂. For both liquidus curves in the system Ca₂SiO₄—CaTiO₃ and for the TiO₂ liquidus curve in the system CaTiSiO₅—TiO₂ better fit of the experimental liquidus curves was achieved when activities were equal to mole fractions.

TiO₂-bearing silicate systems represent important objects of considerable technological and geochemical interest. Titanium dioxide is common component of industrial glasses, enamels, and pyroceramics. It is also a component of some metallurgical slags. Geochemists and petrologists are interested in the influence of titanium on phase equilibria, mineral crystallization sequences, and rheological properties of melts [1]. Titanium-bearing silicate melts and glasses of synthetic and natural composition display unusual behaviour of various physical properties like heat capacity, density, viscosity, thermal expansion coefficient, *etc.* These features may be rationalized in terms of the composition- and temperature-dependent structural role of TiO₂, namely of its network-forming and network-modifying character and changeable oxygen coordination number of Ti⁴⁺ [2].

It is generally known that SiO₂ is the main network-forming oxide in silicate melts. The basic building unit of silicate melts is the tetrahedron SiO₄, where the central silicon atom is coordinated by four oxygen atoms using covalent bonds. In pure silica melt the SiO₄ tetrahedrons are linked into the three-dimensional network using bridging oxygen atoms Si—O—Si. In more complicated systems, besides SiO₂, other oxides, *e.g.* GeO₂, B₂O₃, Al₂O₃, *etc.* can also participate in the formation of the polyanionic network of SiO₄ tetrahedrons.

Alkali metal oxides and earth alkali oxides belong to the so-called modifiers of polyanionic network. In

molten state they contain free cations (*e.g.* Ca²⁺) and free oxygen anions O²⁻. When adding an alkali metal oxide, or an earth alkali oxide, *e.g.* CaO, to SiO₂, each oxygen anion breaks one Si—O—Si bond of the SiO₄ tetrahedral network under formation of two non-bridging oxygen atoms —O⁻ according to the general scheme



Depending on the composition of the system, three types of oxygen atoms may be present in silicate melt: free oxygen anions O²⁻ linked by two ionic bonds to the present alkali cations, nonbridging oxygen atoms —O⁻ linked by one covalent bond to the central Si atom of the SiO₄ tetrahedron and by one ionic bond to the present alkali cation, and finally bridging oxygen atoms —O— connecting two neighbouring SiO₄ tetrahedrons by covalent Si—O—Si bonds. From the above it follows that, with regard to their bonding nature, oxygen atoms are not equivalent, *i.e.* they have not identical chemical potentials.

In the melts of the pseudobinary subsystems of the system CaO—TiO₂—SiO₂, beside silicon oxide, titanium oxide may also participate in the tetrahedral network. Depending on its structural behaviour the structure of the melt may change, causing also a change of activities of present components.

The structural role of Ti⁴⁺ in silicate melts has been the goal of a large assembly of spectroscopic in-

vestigations, *e.g.* [3–7]. It is a complex function of several variables, particularly TiO_2 and SiO_2 concentration, type and content of modifying cations and temperature [6, 8]. Despite the number of investigations, neither a consensus has been reached regarding the coordination states of Ti atoms, nor has it been found how the silicate melt structure is modified by their presence. The results obtained by various methods are often contradictory [5, 7].

In situ high-temperature Raman spectroscopy of melts along the join $\text{Na}_2\text{Si}_2\text{O}_5$ – $\text{Na}_2\text{Ti}_2\text{O}_5$ [6] has shown that the Raman spectra of Ti-bearing glasses and melts are consistent with Ti^{4+} in at least three different structural positions: Ti^{4+} may substitute for Si^{4+} in tetrahedral coordination in the structural units in the melt (it acts as network former), it may form TiO_2 like clusters with Ti^{4+} in tetrahedral coordination (structural role of Ti^{4+} external to the silicate network was proved by NMR data from Ti-bearing aluminosilicate glasses) [5], or it acts as network modifier, possibly occurring in six-fold (octahedral) or five-fold coordination. In vitreous K_2O – TiO_2 – SiO_2 the presence of tetragonal pyramids containing one non-bridging double-bonded oxygen interconnected with SiO_4 tetrahedrons was reported [3].

Density measurements [9, 10] indicate that Ti^{4+} is predominantly in tetrahedral coordination in sodium-bearing liquids, while in octahedral coordination in calcium-bearing melts [9]. Also the compressibility data on alkali and alkaline earth titanium metasilicate melts indicate that the structural role of TiO_2 in these melts is dependent on the identity of the cation [11].

In the present paper the structural behaviour of TiO_2 in the SiO_2 melts is studied indirectly, by means of the theoretical calculation of the phase diagrams of some pseudobinary subsystems of the CaO – TiO_2 – SiO_2 system, using the thermodynamic model of the silicate melts [12, 13], which takes into account the participation of TiO_2 in the SiO_4 tetrahedral network. The results are compared with calculations assuming that activities are identical with mole fractions.

THEORETICAL

According to the used thermodynamic model of silicate melts [12, 13] the chemical potential of the i -th component in a melt can be expressed as a sum of the chemical potentials of all energetically distinguishable j -th atoms constituting the given component. The activity of the first component in a pseudobinary solution of the system CaO – TiO_2 – SiO_2 can be expressed by the equation

$$a_1 = \prod_j \left(\frac{y_j}{y_{1,j}} \right)^{\{n_{1,j}\}} \quad (1)$$

where $y_{1,j}$ and y_j are mole fractions of the j -th atom

(Ca^{2+} , Ti^{4+} , Si^{4+} , O^{2-} , $-\text{O}^-$, $-\text{O}-$) in the pure first component and in the pseudobinary mixture, respectively, defined by the relations

$$y_{1,j} = \frac{n_{1,j}}{\sum_j n_{1,j}} \quad y_j = \frac{x_1 n_{1,j} + x_2 n_{2,j}}{x_1 \sum_j n_{1,j} + x_2 \sum_j n_{2,j}} \quad (2)$$

where x_1 and x_2 are mole fractions of the considered components of the pseudobinary system, $n_{1,j}$ and $n_{2,j}$ are amounts of substance of the j -th atom in the pure first and second component, respectively. Similar relations may be derived also for the second component. $x_1 \sum_j n_{1,j} + x_2 \sum_j n_{2,j} = \sum_j n_j$ is the amount of substance of all present atoms in an arbitrary mixture of both components.

COMPUTATIONAL PROCEDURE

Applying eqns (1) and (2) relations for the activities of the considered components in melts of the studied pseudobinary systems have been derived. These relations take into account structural aspects of melts following from the thermodynamic model. It was assumed that all present titanium substitutes for Si^{4+} in tetrahedral coordination in the structural units of the melt, *i.e.* acts as network former. The calculation of phase diagrams was performed in binary systems CaSiO_3 – CaTiSiO_5 , CaSiO_3 – CaTiO_3 , Ca_2SiO_4 – CaTiO_3 , CaTiSiO_5 – CaTiO_3 , and CaTiSiO_5 – TiO_2 .

The calculation of liquidus temperatures for the individual components $T_{\text{liq},i}$ was performed using the simplified and adapted LeChatelier–Shreder equation [14]

$$T_{\text{liq},i} = \frac{\Delta_{\text{fus}} H_i T_{\text{fus},i}}{\Delta_{\text{fus}} H_i - RT_{\text{fus},i} \ln a_i} \quad (3)$$

where $T_{\text{fus},i}$ and $\Delta_{\text{fus}} H_i$ are temperature and enthalpy of fusion of the i -th solid phase, respectively, and a_i is its activity in the melt, calculated according to corresponding form of eqn (1). The needed thermodynamic quantities, *i.e.* temperatures and enthalpies of fusion of the individual phases, taken from literature, are listed in Table 1.

The phase diagrams of the considered pseudobinary systems have been constructed on the basis of calculated values of temperatures of primary crystallization of the individual phases with the composition steps $\Delta x_i = 0.1$. The positions of eutectic points have been obtained as intersection points of both liquidus curves. Experimental phase diagrams were taken from papers [15, 16].

Table 1. Temperatures and Enthalpies of Fusion of Pure Substances Used in the Calculation

Compound	T_{fus} K	$\Delta_{\text{fus}}H$ kJ mol ⁻¹	Ref.
CaO	2843	52.0	[18, 19]
Ca ₂ SiO ₄	2403	55.4	[18, 19]
CaSiO ₃	1817	56.0	[18, 19]
CaTiSiO ₅	1656	139.0	[17]
CaTiO ₃	2243	127.3*	Estimated
TiO ₂	2103	66.9	[18, 19]
SiO ₂	1986	9.6	[7, 8]

* $\Delta_{\text{fus}}H_{\text{CaTiO}_3} = T_{\text{fus,CaTiO}_3} \Delta_{\text{fus}}S_{\text{MgTiO}_3}$.

RESULTS AND DISCUSSION

a) System CaSiO₃—CaTiSiO₅

Let us consider x_1 and x_2 to be the mole fractions of CaSiO₃ and CaTiSiO₅, respectively, in a binary mixture of both components. The amount of substance of all present atoms in an arbitrary mixture in this system is $\sum n_j = (5x_1 + 8x_2)$ mol and the amount of substance of all oxygen atoms in this system is $n(\text{O}) = (3x_1 + 5x_2)$ mol. Assuming that all the TiO₂ present in the system acts as network former, the amount of substance of Si,Ti—O bonds is equal to $n(\text{Si,Ti—O}) = (4x_1 + 8x_2)$ mol. In the pure CaSiO₃ one of three oxygen atoms is bridging while the other two atoms are nonbridging. On the other hand, in the pure CaTiSiO₅ there are two nonbridging and three bridging oxygen atoms. Hence, there are $n(\text{—O—}) = (x_1 + 3x_2)$ mol of bridging oxygen atoms and $n(\text{—O}^-) = (2x_1 + 2x_2)$ mol of nonbridging oxygen atoms in the mixture. For the CaSiO₃ activity we obtain the expression

$$a(\text{CS}) = \left(\frac{x_1 + x_2}{0.2 \sum \{n_j\}} \right) \left(\frac{x_1 + x_2}{0.2 \sum \{n_j\}} \right) \cdot \left(\frac{2x_1 + 2x_2}{0.4 \sum \{n_j\}} \right)^2 \left(\frac{x_1 + 3x_2}{0.2 \sum \{n_j\}} \right) \quad (4)$$

and for the CaTiSiO₅ activity the expression

$$a(\text{CTS}) = \left(\frac{x_1 + x_2}{0.125 \sum \{n_j\}} \right) \left(\frac{x_2}{0.125 \sum \{n_j\}} \right) \cdot \left(\frac{x_1 + x_2}{0.125 \sum \{n_j\}} \right) \left(\frac{2x_1 + 2x_2}{0.25 \sum \{n_j\}} \right)^2 \left(\frac{x_1 + 3x_2}{0.375 \sum \{n_j\}} \right)^3 \quad (5)$$

The comparison of experimental and calculated phase diagrams of the system CaSiO₃—CaTiSiO₅ is given in Fig. 1a. The solid solutions in the composition range

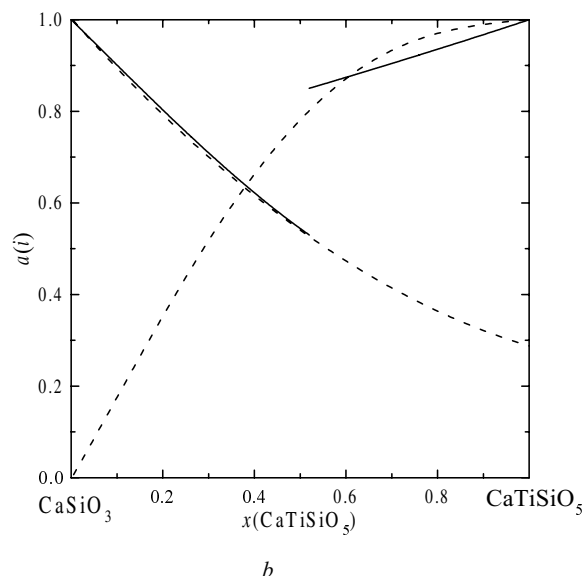
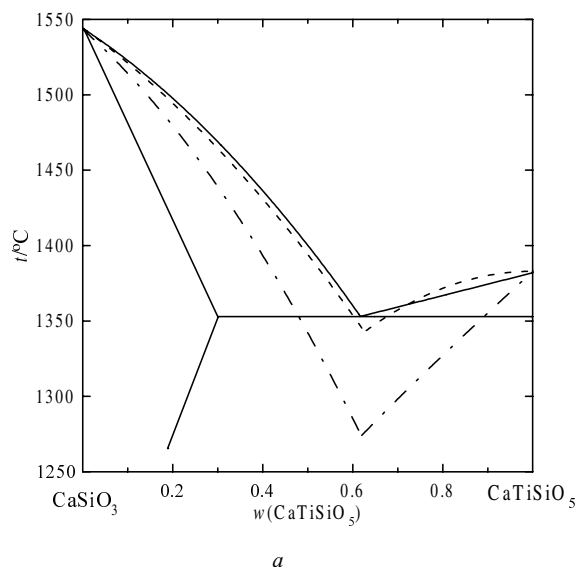


Fig. 1. Phase diagram a) and activities of components b) of the system CaSiO₃—CaTiSiO₅. Solid line: experiment [15], dashed line: thermodynamic model [12, 13], dot-dashed line: $a_i = x_i$.

up to $x(\text{CS}_{\text{ss}}) = 0.3$ at the eutectic temperature were assumed by calculation of the CaSiO₃ liquidus curve. For comparison liquidus curves calculated on the assumption that activities of both components are equal to mole fractions are also presented in Fig. 1a. It can be seen in this figure that used thermodynamic model fits the experimental data better than assumption $a_i = x_i$. Similar conclusion follows from the activity curves of individual components of the considered system (Fig. 1b), calculated using experimental phase diagram (solid line) and thermodynamic model according to eqn (1) (dashed line).

b) System CaSiO_3 — CaTiO_3

Considering x_1 and x_2 to be the mole fractions of CaSiO_3 and CaTiO_3 , respectively, the amount of substance of all present atoms in an arbitrary mixture in this system is $\sum n_j = (5x_1 + 5x_2)$ mol, and the amount of substance of all oxygen atoms is $n(\text{O}) = (3x_1 + 3x_2)$ mol. On the above assumption concerning the role of the TiO_2 in the melt the amount of substance of Si,Ti—O bonds is $n(\text{Si,Ti—O}) = (4x_1 + 4x_2)$ mol. Similarly as in CaSiO_3 , in CaTiO_3 there are also two nonbridging oxygen atoms and one bridging oxygen atom. The amount of substance of bridging oxygen atoms in the mixture is $n(\text{—O—}) = (x_1 + x_2)$ mol, while the amount of substance of nonbridging oxygen atoms is $n(\text{—O}^-) = (2x_1 + 2x_2)$ mol. For the activity of CaSiO_3 we obtain the expression

$$a(\text{CS}) = \left(\frac{x_1 + x_2}{0.2 \sum \{n_j\}} \right) \left(\frac{x_1}{0.2 \sum \{n_j\}} \right) \cdot \left(\frac{2x_1 + 2x_2}{0.4 \sum \{n_j\}} \right)^2 \left(\frac{x_1 + x_2}{0.2 \sum \{n_j\}} \right) \quad (6)$$

and for the activity of CaTiO_3 we can write

$$a(\text{CT}) = \left(\frac{x_1 + x_2}{0.2 \sum \{n_j\}} \right) \left(\frac{x_2}{0.2 \sum \{n_j\}} \right) \cdot \left(\frac{2x_1 + 2x_2}{0.4 \sum \{n_j\}} \right)^2 \left(\frac{x_1 + x_2}{0.2 \sum \{n_j\}} \right) \quad (7)$$

After inserting the general relation $x_1 + x_2 = 1$ into eqns (6) and (7) one can see that in this case the thermodynamic model is identical with $a_i = x_i$ model. It can be seen in the phase diagram of this system shown in Fig. 2a that in the frame of uncertainty of regression both liquidus curves are identical for both models. The experimental liquidus curve for CaTiO_3 is not thermodynamically consistent, because in the region of the melting point it has dystectic course, which is not probable with regard to the nature of this compound. Similar conclusion follows also from the activity curve of CaTiO_3 in the region of the pure component (see Fig. 2b), calculated on the basis of the experimental phase diagram.

c) System Ca_2SiO_4 — CaTiO_3

In the system Ca_2SiO_4 — CaTiO_3 the amount of substance of all present atoms in an arbitrary mixture is $\sum n_j = (7x_1 + 5x_2)$ mol and the amount of substance of all oxygen atoms is $n(\text{O}) = (4x_1 + 3x_2)$ mol. The amount of substance of Si,Ti—O bonds is $n(\text{Si,Ti—O}) = (4x_1 + 4x_2)$ mol. In the pure Ca_2SiO_4 all oxygen atoms are nonbridging. The amount of substance of bridging oxygen atoms in the mixture is $n(\text{—O—}) = x_2$ mol and the amount of substance of

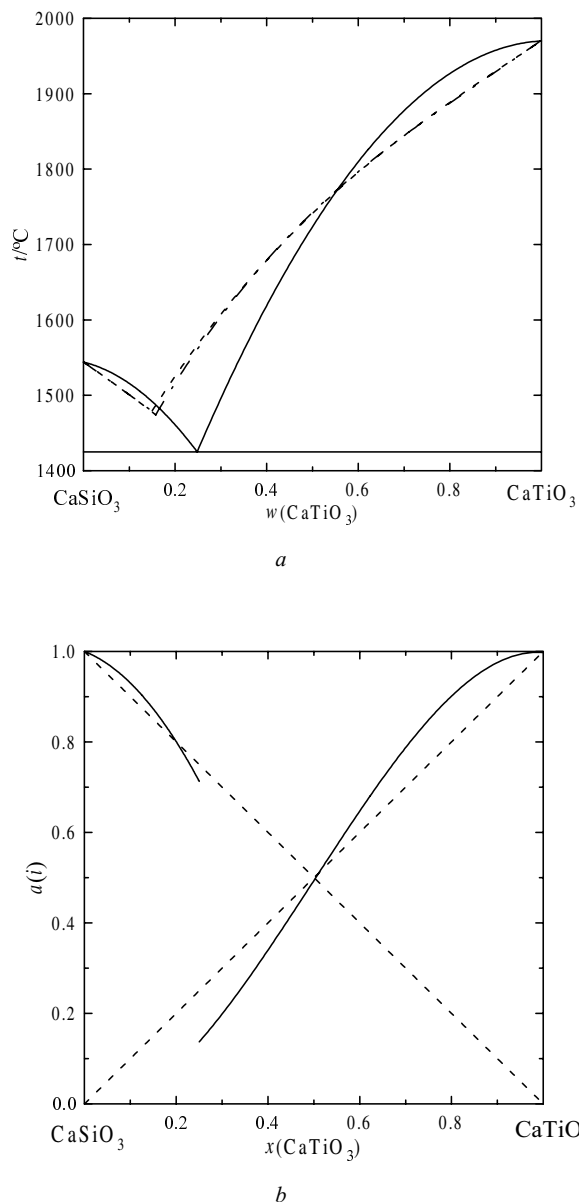


Fig. 2. Phase diagram a) and activities of components b) of the system CaSiO_3 — CaTiO_3 . Denotation as in Fig. 1.

nonbridging oxygen atoms is $n(\text{—O}^-) = (4x_1 + 2x_2)$ mol. For the activity of Ca_2SiO_4 we obtain the expression

$$a(\text{C}_2\text{S}) = \left(\frac{2x_1 + x_2}{0.286 \sum \{n_j\}} \right)^2 \left(\frac{x_1}{0.143 \sum \{n_j\}} \right) \cdot \left(\frac{4x_1 + 2x_2}{0.571 \sum \{n_j\}} \right)^4 \quad (8)$$

and for the activity of CaTiO_3 we can write

$$a(\text{CT}) = \left(\frac{2x_1 + x_2}{0.2 \sum \{n_j\}} \right) \left(\frac{x_2}{0.2 \sum \{n_j\}} \right) \cdot \left(\frac{4x_1 + 2x_2}{0.4 \sum \{n_j\}} \right)^2 \left(\frac{x_2}{0.2 \sum \{n_j\}} \right) \quad (9)$$

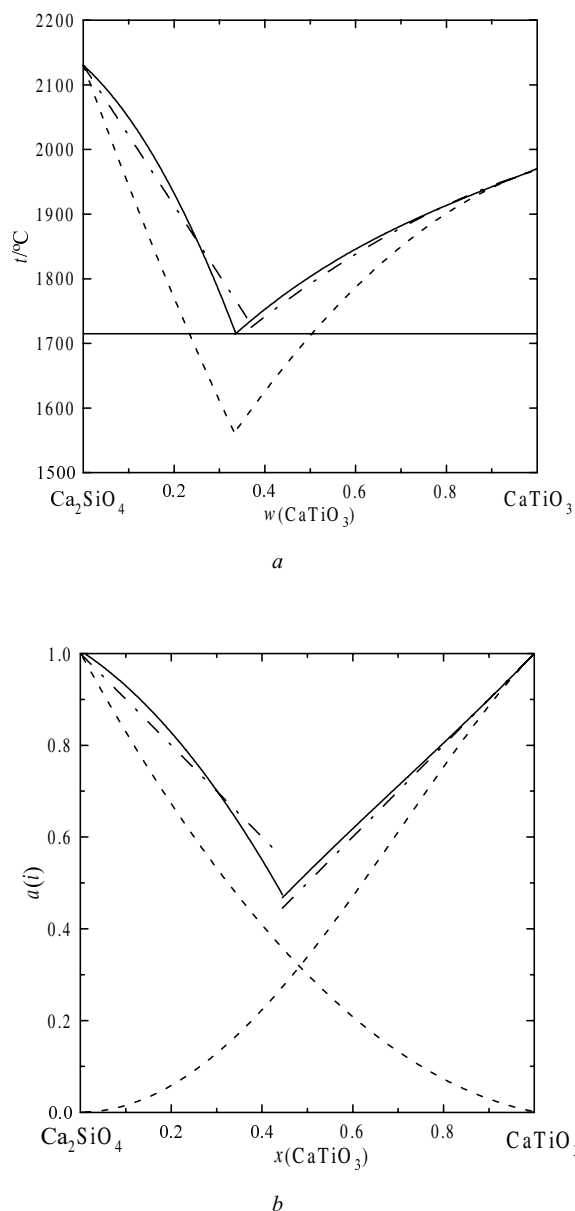


Fig. 3. Phase diagram *a*) and activities of components *b*) of the system Ca₂SiO₄—CaTiO₃. Solid line: experiment [16], dashed line: thermodynamic model [12, 13], dot-dashed line: $a_i = x_i$.

The phase diagram of the system Ca₂SiO₄—CaTiO₃ is presented in Fig. 3a. It can be seen in this figure that calculation corresponding to the $a_i = x_i$ assumption fits the experimental data best. This subsystem of the CaO—TiO₂—SiO₂ system is in the alkaline region of melts, where the model fails. Similar conclusion follows also from the activities presented in Fig. 3b.

d) System CaTiSiO₅—CaTiO₃

In this system the amount of substance of all present atoms in an arbitrary mixture is $\sum n_j = (8x_1 + 5x_2)$ mol, the amount of substance of all oxy-

gen atoms is $n(\text{O}) = (5x_1 + 3x_2)$ mol, and the amount of substance of Si,Ti—O bonds is $n(\text{Si,Ti—O}) = (8x_1 + 4x_2)$ mol. The amount of substance of bridging oxygen atoms in the mixture is $n(\text{—O—}) = (3x_1 + x_2)$ mol and the amount of substance of non-bridging oxygen atoms in the mixture is $n(\text{—O}^-) = (2x_1 + 2x_2)$ mol. For the activity of CaTiSiO₅ we obtain the expression

$$a(\text{CTS}) = \left(\frac{x_1 + x_2}{0.125 \sum \{n_j\}} \right) \left(\frac{x_1 + x_2}{0.125 \sum \{n_j\}} \right) \cdot \left(\frac{x_1}{0.125 \sum \{n_j\}} \right) \left(\frac{2x_1 + 2x_2}{0.25 \sum \{n_j\}} \right)^2 \left(\frac{3x_1 + x_2}{0.375 \sum \{n_j\}} \right)^3 \quad (10)$$

and the activity of CaTiO₃ is given by the equation

$$a(\text{CT}) = \left(\frac{x_1 + x_2}{0.2 \sum \{n_j\}} \right) \left(\frac{x_1 + x_2}{0.2 \sum \{n_j\}} \right) \cdot \left(\frac{2x_1 + 2x_2}{0.4 \sum \{n_j\}} \right)^2 \left(\frac{3x_1 + x_2}{0.2 \sum \{n_j\}} \right) \quad (11)$$

The comparison of experimental and calculated phase diagrams of this system is given in Fig. 4a. With regard to the big difference between temperature of fusion of CaTiO₃ and eutectic temperature, the temperature dependence of the enthalpy of fusion of this compound has been taken into account by calculation of the liquidus curve introducing the heat capacity of fusion $\Delta_{\text{fus}}C_p(\text{CT}) = 250 \text{ J mol}^{-1} \text{ K}^{-1}$. From the figure it follows that the thermodynamic model of silicate melts describes the phase diagram of this system very well. This is also confirmed by activities of components in this system (Fig. 4b).

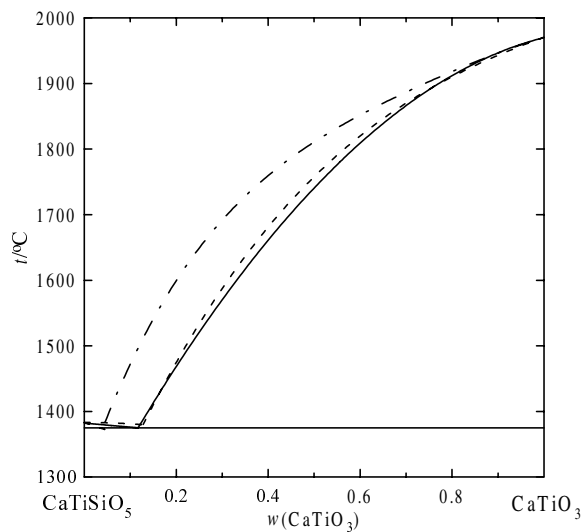
e) System CaTiSiO₅—TiO₂

In the system CaTiSiO₅—TiO₂ the amount of substance of all present atoms in an arbitrary mixture is $\sum n_j = (8x_1 + 3x_2)$ mol, the amount of substance of all oxygen atoms is $n(\text{O}) = (5x_1 + 2x_2)$ mol and the amount of substance of Si,Ti—O bonds is $n(\text{Si,Ti—O}) = (8x_1 + 4x_2)$ mol. The amount of substance of bridging and nonbridging oxygen atoms in the mixture is $n(\text{—O—}) = (3x_1 + 2x_2)$ mol and $n(\text{—O}^-) = 2x_1$ mol, respectively. For the activity of CaTiSiO₅ we obtain the expression

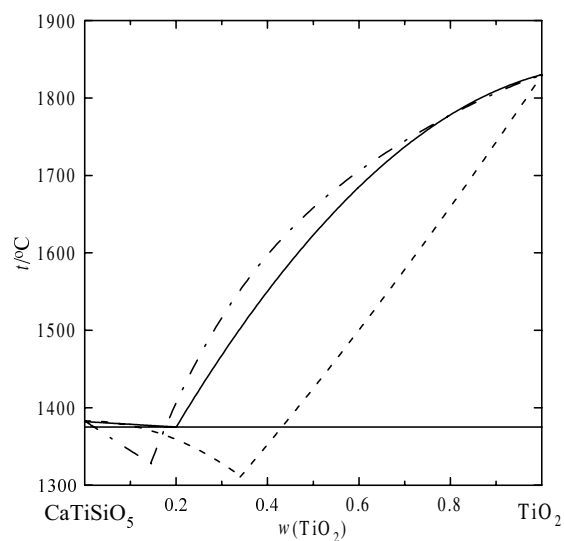
$$a(\text{CTS}) = \left(\frac{x_1}{0.125 \sum \{n_j\}} \right) \left(\frac{x_1 + x_2}{0.125 \sum \{n_j\}} \right) \cdot \left(\frac{x_1}{0.125 \sum \{n_j\}} \right) \left(\frac{2x_1}{0.25 \sum \{n_j\}} \right)^2 \left(\frac{3x_1 + 2x_2}{0.375 \sum \{n_j\}} \right)^3 \quad (12)$$

and the activity of TiO₂ is equal to

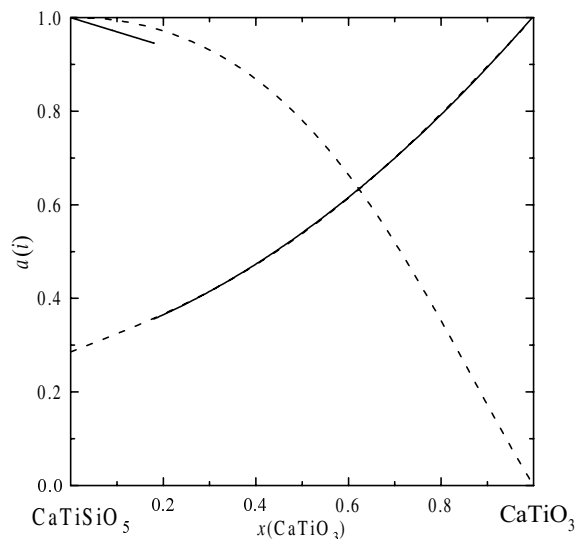
$$a(\text{T}) = \left(\frac{x_1 + x_2}{0.333 \sum \{n_j\}} \right) \left(\frac{3x_1 + 2x_2}{0.667 \sum \{n_j\}} \right)^2 \quad (13)$$



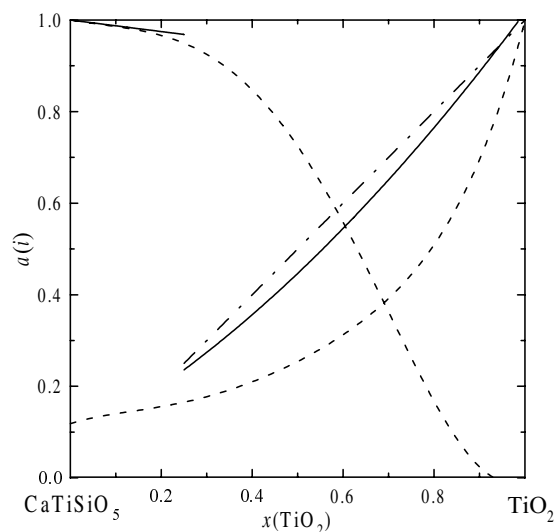
a



a



b



b

Fig. 4. Phase diagram a) and activities of components b) of the system $\text{CaTiSiO}_5\text{—CaTiO}_3$. Denotation as in Fig. 1.

Fig. 5. Phase diagram a) and activities of components b) of the system $\text{CaTiSiO}_5\text{—TiO}_2$. Denotation as in Fig. 1.

The phase diagram of the system $\text{CaTiSiO}_5\text{—TiO}_2$ is shown in Fig. 5a. As it can be seen in this figure, the liquidus curve of CaTiSiO_5 is described well by the used thermodynamic model while the experimental liquidus curve of TiO_2 is fitted best by the simple $a_i = x_i$ model. The reason is probably the alkaline nature of the TiO_2 -rich melts again. Similar conclusion follows also from the activities presented in Fig. 5b.

CONCLUSION

The comparison of experimental and calculated phase diagrams of the system $\text{CaSiO}_3\text{—CaTiSiO}_5$ (Fig. 1a) shows that the model of the titanium-bearing

silicate melts, based on the assumption that all the present TiO_2 acts as network former fits the experimental liquidus curves very good on the assumption that solid solutions in the composition range up to $x(\text{CS}_{\text{ss}}) = 0.3$ at the eutectic temperature are considered at calculation of the CaSiO_3 liquidus curve. However, this assumption was not confirmed experimentally.

In the system $\text{CaSiO}_3\text{—CaTiO}_3$ (Fig. 2a) there is no significant difference between liquidus curves calculated by the use of both considered models, due to identity of both models for this system. The small discrepancy between both liquidus curves in Fig. 2a is due to the uncertainty of regression, used at drawing of

both curves. Nevertheless, the experimental data are not fitted well. Remark that the experimental liquidus curve of CaTiO₃ is not thermodynamically consistent in the region of the melting point, because it shows dystectic character. However, the dystectic melting is not probable with regard to the nature of this compound.

Both liquidus curves in the Ca₂SiO₄—CaTiO₃ phase diagram (Fig. 3a) and the liquidus curve of TiO₂ in the CaTiSiO₅—TiO₂ phase diagram (Fig. 5a) are fitted quite well with the simple assumption $a_i = x_i$. The tested model, however, does not match the experimental data satisfactorily. The reason may be in the alkaline nature of the TiO₂-rich melts, where the tested model fails. On the other hand, the thermodynamic model describes best the liquidus curve of CaTiSiO₅ in the CaTiSiO₅—TiO₂ system.

Due to the relatively big difference between temperature of fusion of CaTiO₃ and eutectic temperature in the CaTiSiO₅—CaTiO₃ system the temperature dependence of the enthalpy of fusion of CaTiO₃ was taken into account at calculation of its liquidus curve, introducing the heat capacity of fusion $\Delta_{\text{fus}}C_p(\text{CT}) = 250 \text{ J mol}^{-1}\text{K}^{-1}$. In this case the thermodynamic model of silicate melts describes the phase diagram of this system very well.

The results indicate that the basic premise implemented into the considered thermodynamic model, namely that TiO₂ is completely included in the structural network in the form of tetrahedrally coordinated units, is fulfilled in the systems CaSiO₃—CaTiSiO₅ and CaTiSiO₅—CaTiO₃, while it is not satisfied in the systems Ca₂SiO₄—CaTiO₃, CaSiO₃—CaTiO₃, and CaTiSiO₅—TiO₂. This conclusion is in good agreement with spectroscopic data, and density and compressibility measurements.

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