

# Phase Diagram and Structure of Melts of the System CaO—TiO<sub>2</sub>—SiO<sub>2</sub>

V. DANĚK and I. NERÁD

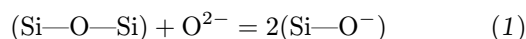
*Institute of Inorganic Chemistry, Slovak Academy of Sciences, SK-842 36 Bratislava  
e-mail: uachdane@savba.sk*

Received 18 December 2000  
Accepted for publication 12 June 2002

Phase diagrams of the systems CaO—TiO<sub>2</sub> and CaO—TiO<sub>2</sub>—SiO<sub>2</sub> were calculated using thermodynamic model of silicate melts. The calculated phase diagrams fit the experimentally determined ones well, assuming that the present TiO<sub>2</sub> behaves as network-forming oxide in the prevailing concentration region of the ternary system. For the better fit in the CaO-, TiO<sub>2</sub>-, and SiO<sub>2</sub>-rich concentration regions, the activities of these components were set to be equal to their mole fraction. This means that in the prevailing concentration region of the ternary system TiO<sub>2</sub> participates in the formation of the polyanionic network.

It is generally known that SiO<sub>2</sub> is the main network-forming oxide in the structure of silicate melts. The basic building unit of the silicate melts is the tetrahedron SiO<sub>4</sub>, where the central silicon atom is bound to four oxygen atoms by covalent bonds. In the melt of pure silicon oxide the SiO<sub>4</sub> tetrahedrons are linked together into a three-dimensional space network using the bridging oxygen —O— atoms. Beside SiO<sub>2</sub>, other oxides, like *e.g.* GeO<sub>2</sub>, B<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub>, *etc.* may participate in the formation of the polyanionic network. Under certain circumstances also TiO<sub>2</sub> can contribute to the formation of the tetrahedral network.

Oxides of alkali and earth alkali metals belong to the so-called modifiers of the polyanionic network. In molten state they contain free cations (*e.g.* Ca<sup>2+</sup>) and free anions O<sup>2-</sup>. When adding an alkali or earth alkali metal oxide, *e.g.* CaO, to SiO<sub>2</sub>, each oxide anion breaks one of the Si—O—Si bonds under formation of two nonbridging —O<sup>-</sup> oxygen atoms according to the general scheme



Depending on the total composition of the system, the oxygen atoms may play various roles in the silicate melts: Present as free oxygen anions O<sup>2-</sup> they are bound by two ionic bonds to the present alkali or earth alkali cations. In the role of nonbridging oxygen atoms —O<sup>-</sup> they are bound by one covalent bond to the central atom of the SiO<sub>4</sub> tetrahedron and by one ionic bond to the present alkali or earth alkali metal cation. And finally, as bridging oxygen atoms —O— they are binding two neighbouring SiO<sub>4</sub> tetrahedrons

by Si—O—Si covalent bonds. From the above it follows that with respect to their bonding nature, oxygen atoms are not equivalent, *i.e.* their chemical potentials are not equal.

In melts of the ternary system CaO—TiO<sub>2</sub>—SiO<sub>2</sub> silicon oxide acts always as the network-forming oxide and calcium oxide acts always as the modifier of the polyanionic network. As it was already mentioned above, TiO<sub>2</sub> can act as the modifier or it can play the role of the network-forming oxide. Depending on the behaviour of TiO<sub>2</sub> in the melt the structure and thus also the activities of the present components of the melt change.

The structural role of Ti<sup>4+</sup> in titanium silicate melts is a complex function of several variables, namely TiO<sub>2</sub> and SiO<sub>2</sub> concentration, type and content of modifying cations, and temperature [1, 2]. Despite of number of investigations a consensus has not been reached regarding coordination states of Ti atoms and their influence on the structure of the silicate melts. The results obtained by various methods are often contradictory [3, 4].

The presence of TiO<sub>2</sub> in silicate liquids has a profound influence on the heat capacity of simple three-component silicate liquids over the temperature range 900—1300 K [2]. *Richet* and *Bottinga* [5] observed that the heat capacity of alkali-titanium silicate melts displays complex negative temperature dependence. The replacement of Si<sup>4+</sup> by Ti<sup>4+</sup> leads to doubling of the magnitude of the jump in  $C_p$  at the glass transition. This is followed by a progressive decrease in liquid  $C_p$  for over 400 K until  $C_p$  eventually becomes constant and similar to that in Ti-free systems. The large  $C_p$  step at  $T_g$  in the TiO<sub>2</sub>-bearing melts suggests signifi-

cant configurational rearrangements in the liquid that are not available in TiO<sub>2</sub>-free silicates. These configurational changes apparently saturate as temperature increases. Above 1400 K, however, where the heat capacities of TiO<sub>2</sub>-bearing and TiO<sub>2</sub>-free alkali silicate liquids are similar, their configurational entropies differ by about 3.5 J mol<sup>-1</sup> K<sup>-1</sup>. This is energetically equivalent to raising the temperature of liquid by more than 300 K. This demonstrates the energetic magnitude of the configurational changes apparent in the supercooled liquid region and their impact on the thermodynamic properties of the stable liquid [2].

The calculation of phase diagrams of the CaO—TiO<sub>2</sub>—SiO<sub>2</sub> system on the basis of available experimental data has been the goal of several studies. Various types of models for the thermodynamic properties of the liquid phase have been used. In [6] the critical evaluation and optimization of the CaO—TiO<sub>2</sub>—SiO<sub>2</sub> system phase diagram by the use of the thermodynamic properties of the component oxides and of the modified quasichemical model for the excess Gibbs energy of the liquid phase was presented. The generalization of an extrapolation formula of *Kohler* [7] for the excess Gibbs energy of the liquid phase was found to be suitable to describe the immiscibility gap in the phase diagram of the CaO—TiO<sub>2</sub>—SiO<sub>2</sub> system by *DeCapitani* and *Kirschen* [8, 9].

In the present paper the structural behaviour of TiO<sub>2</sub> was evaluated by means of the theoretical calculation of the phase diagrams of the CaO—TiO<sub>2</sub> and CaO—TiO<sub>2</sub>—SiO<sub>2</sub> systems using the thermodynamic model of the silicate melts [10, 11], taking into account the participation of TiO<sub>2</sub> in the polyanionic network.

## THEORETICAL

Let us consider a mixture with the composition of  $a$  mol CaO +  $b$  mol TiO<sub>2</sub> +  $c$  mol SiO<sub>2</sub>. The amount of all oxygen atoms in an arbitrary mixture is  $n(\text{O}) = (a + 2b + 2c)$  mol and the amount of all present atoms is  $\sum n_{i,j} = (2a + 3b + 3c)$  mol. Two different situations can happen with respect to the total composition of the mixture.

In the region of basic melts, *i.e.* at high CaO content, only free oxide anions O<sup>2-</sup> and nonbridging oxygen atoms are present in the mixture. The total material balance of the oxygen atoms is given by the equation

$$n(\text{O}) = n(\text{O}^{2-}) + n(\text{—O}^-) \quad (2)$$

If only SiO<sub>2</sub> participates in the formation of the polyanionic network, the amount of Si—O bonds and equally also the amount of nonbridging oxygen atoms in the mixture is  $n(\text{Si—O}) = n(\text{—O}^-) = 4c$  mol and the amount of oxide anions is  $n(\text{O}^{2-}) = (a + 2b + 2c - 4c)$  mol =  $(a + 2b - 2c)$  mol. In the case, when also all present TiO<sub>2</sub> behaves as network-forming oxide, the

amount of Si—O and Ti—O bonds and equally also the amount of nonbridging oxygen atoms in the mixture is  $n(\text{Si, Ti—O}) = n(\text{—O}^-) = (4b + 4c)$  mol and the amount of oxide anions is  $n(\text{O}^{2-}) = (a + 2b + 2c - (4b + 4c))$  mol =  $(a - 2b - 2c)$  mol.

In the region of acidic melts, *i.e.* at medium and high SiO<sub>2</sub> content only nonbridging and bridging oxygen atoms are present in the mixture and the total material balance of oxygen atoms is given by the equation

$$n(\text{O}) = n(\text{—O—}) + n(\text{—O}^-) \quad (3)$$

Assuming that all present TiO<sub>2</sub> behaves as the modifier of the polyanionic network, exclusively Si—O bonds of the SiO<sub>4</sub> tetrahedrons participate in its formation. The amount of bridging oxygen atoms will then be  $n(\text{—O—}) = (4c - (a + 2b + 2c))$  mol =  $(2c - a - 2b)$  mol and the amount of nonbridging oxygen atoms will be  $n(\text{—O}^-) = (a + 2b + 2c - (2c - a - 2b))$  mol =  $(2a + 4b)$  mol. In the case, when all TiO<sub>2</sub> is network-forming, the amount of Si—O and Ti—O bonds in the SiO<sub>4</sub> and TiO<sub>4</sub> tetrahedrons will be  $n(\text{Si, Ti—O}) = (4b + 4c)$  mol. The amount of bridging oxygen atoms equals to  $n(\text{—O—}) = (4b + 4c - (a + 2b + 2c))$  mol =  $(2b + 2c - a)$  mol and the amount of nonbridging oxygen atoms equals to  $n(\text{—O}^-) = 2a$  mol.

According to the considered model [10, 11] the activity of  $i$ -th component in the mixture is given by the expression

$$a_i = \prod_{j=1}^k \left( \frac{y_j}{y_{i,j}^{\circ}} \right)^{\{n_{i,j}^{\circ}\}} \quad (4)$$

where  $y_{i,j}^{\circ}$  and  $y_j$  are the mole fractions of  $j$ -th atoms (Ca<sup>2+</sup>, Ti<sup>4+</sup>, Si<sup>4+</sup>, O<sup>2-</sup>, —O<sup>-</sup>, —O—) in the pure  $i$ -th component and in the mixture, respectively, defined by the relations

$$y_{i,j}^{\circ} = \frac{n_{i,j}^{\circ}}{\sum_j n_{i,j}^{\circ}} \quad y_j = \frac{\sum_i n_{i,j} x_i}{\sum_i x_i \sum_j n_{i,j}} \quad (5)$$

$x_i = a, b, c$  are the mole fractions of the basic components of the system (CaO, TiO<sub>2</sub>, SiO<sub>2</sub>),  $n_{i,j}^{\circ}$  and  $n_{i,j}$  are the amounts of the  $j$ -th atoms in the individual pure phases and in the mixture, respectively.

In the phase diagram of the system CaO—TiO<sub>2</sub>—SiO<sub>2</sub> the following phases are present: CaO, TiO<sub>2</sub>, SiO<sub>2</sub>, Ca<sub>3</sub>SiO<sub>5</sub>, Ca<sub>2</sub>SiO<sub>4</sub>, Ca<sub>3</sub>Si<sub>2</sub>O<sub>7</sub>, CaSiO<sub>3</sub>, CaTiO<sub>3</sub>, Ca<sub>3</sub>Ti<sub>2</sub>O<sub>7</sub>, and CaTiSiO<sub>5</sub>. With respect to the very narrow regions of the primary crystallization of Ca<sub>3</sub>SiO<sub>5</sub> and Ca<sub>3</sub>Si<sub>2</sub>O<sub>7</sub>, their presence was not taken into account in the calculation. In the following paragraphs the relations for the activity of phases, considered to be present in the melts of the CaO—TiO<sub>2</sub>—SiO<sub>2</sub> system, are given under application of eqns (4) and (5) according to the thermodynamic model assuming the network-forming character of TiO<sub>2</sub>.

**a) CaO**

Only cations Ca<sup>2+</sup> and anions O<sup>2-</sup> are present in the formula unit of CaO (C). Assuming that the present TiO<sub>2</sub> behaves as the network-forming oxide, for the activity of CaO we obtain the expression

$$a(\text{C}) = \left( \frac{a}{0.5 \sum n_{i,j}} \right) \left( \frac{a - 2b - 2c}{0.5 \sum n_{i,j}} \right) \quad (6)$$

If the amount of oxide anions attains zero, the activity of CaO will be zeroing as well.

**b) Ca<sub>2</sub>SiO<sub>4</sub>**

In the formula unit of Ca<sub>2</sub>SiO<sub>4</sub> (C<sub>2</sub>S), dicalcium silicate, all the present oxygen atoms are nonbridging ones. In the case, when all the present TiO<sub>2</sub> in an arbitrary mixture behaves as network-forming oxide, the activity of Ca<sub>2</sub>SiO<sub>4</sub> in the basic composition region is given by the equation

$$a(\text{C}_2\text{S}) = \left( \frac{a}{0.286 \sum n_{i,j}} \right)^2 \left( \frac{c}{0.143 \sum n_{i,j}} \right) \cdot \left( \frac{4b + 4c}{0.571 \sum n_{i,j}} \right)^4 \quad (7a)$$

while in the acidic composition region the activity of Ca<sub>2</sub>SiO<sub>4</sub> was calculated according to the equation

$$a(\text{C}_2\text{S}) = \left( \frac{a}{0.286 \sum n_{i,j}} \right)^2 \left( \frac{c}{0.143 \sum n_{i,j}} \right) \cdot \left( \frac{2a}{0.571 \sum n_{i,j}} \right)^4 \quad (7b)$$

**c) CaSiO<sub>3</sub>**

In the formula unit of CaSiO<sub>3</sub> (CS), wollastonite, there is one bridging and two nonbridging oxygen atoms. In the case, when all the present TiO<sub>2</sub> behaves as network-forming oxide, the activity of CaSiO<sub>3</sub> is given by the equation

$$a(\text{CS}) = \left( \frac{a}{0.2 \sum n_{i,j}} \right) \left( \frac{c}{0.2 \sum n_{i,j}} \right) \cdot \left( \frac{2a}{0.4 \sum n_{i,j}} \right)^2 \left( \frac{2b + 2c - a}{0.2 \sum n_{i,j}} \right) \quad (8)$$

**d) CaTiSiO<sub>5</sub>**

When all the present TiO<sub>2</sub> is network-forming, three oxygen atoms in the pure CaTiSiO<sub>5</sub> (CTS) will

be bridging and two oxygen atoms will be nonbridging ones. For the activity of CaTiSiO<sub>5</sub> we then get the equation

$$a(\text{CTS}) = \left( \frac{a}{0.125 \sum n_{i,j}} \right) \left( \frac{b}{0.125 \sum n_{i,j}} \right) \cdot \left( \frac{c}{0.125 \sum n_{i,j}} \right) \left( \frac{2a}{0.25 \sum n_{i,j}} \right)^2 \cdot \left( \frac{2b + 2c - a}{0.375 \sum n_{i,j}} \right)^3 \quad (9)$$

**e) Ca<sub>3</sub>Ti<sub>2</sub>O<sub>7</sub>**

In the case, when all the present TiO<sub>2</sub> is network-forming, in the formula unit of Ca<sub>3</sub>Ti<sub>2</sub>O<sub>7</sub> (C<sub>3</sub>T<sub>2</sub>) there are one bridging oxygen atom and six nonbridging ones. For the activity of Ca<sub>3</sub>Ti<sub>2</sub>O<sub>7</sub> we obtain the relation

$$a(\text{C}_3\text{T}_2) = \left( \frac{a}{0.25 \sum n_{i,j}} \right)^3 \left( \frac{b}{0.167 \sum n_{i,j}} \right)^2 \cdot \left( \frac{2a}{0.5 \sum n_{i,j}} \right)^6 \left( \frac{2b + 2c - a}{0.083 \sum n_{i,j}} \right) \quad (10)$$

**f) CaTiO<sub>3</sub>**

CaTiO<sub>3</sub> (CT), perovskite, is a mixed oxide with characteristic structure in solid state. In molten state, however, the structure depends on the behaviour of TiO<sub>2</sub>. When this oxide behaves as a network-forming one, the situation is similar like in the wollastonite, *i.e.* in the pure perovskite there is one bridging oxygen atom and two nonbridging ones. For the activity of CaTiO<sub>3</sub> we get the expression

$$a(\text{CT}) = \left( \frac{a}{0.2 \sum n_{i,j}} \right) \left( \frac{b}{0.2 \sum n_{i,j}} \right) \cdot \left( \frac{2a}{0.4 \sum n_{i,j}} \right)^2 \left( \frac{2b + 2c - a}{0.2 \sum n_{i,j}} \right) \quad (11)$$

**g) TiO<sub>2</sub>**

When TiO<sub>2</sub> behaves as a network-forming oxide, the situation is similar like in pure SiO<sub>2</sub>. For the activity of TiO<sub>2</sub> (T) we get the equation

$$a(\text{T}) = \left( \frac{b}{0.333 \sum n_{i,j}} \right) \left( \frac{2b + 2c - a}{0.667 \sum n_{i,j}} \right)^2 \quad (12)$$

h) SiO<sub>2</sub>

In pure molten SiO<sub>2</sub> (S) only bridging oxygen atoms are present. For the activity of SiO<sub>2</sub>, when all the present TiO<sub>2</sub> in an arbitrary mixture of the system CaO—TiO<sub>2</sub>—SiO<sub>2</sub> behaves as network-forming, we can derive the relation

$$a(S) = \left( \frac{c}{0.333 \sum n_{i,j}} \right) \left( \frac{2b + 2c - a}{0.667 \sum n_{i,j}} \right)^2 \quad (13)$$

## COMPUTATIONAL PROCEDURE

In the calculation of the phase diagram of the ternary system CaO—TiO<sub>2</sub>—SiO<sub>2</sub> the main emphasis was laid to the behaviour of TiO<sub>2</sub> and the coordination of the Ti(IV) atoms. The phase diagram was constructed on the basis of the thermodynamic model of silicate melts. In the calculation of the temperatures of the primary crystallization of individual phases the figurative points in the whole composition range  $x(\text{TiO}_2) \in (0; 1)$  and  $x(\text{SiO}_2) \in (0; 1)$  with the step  $\Delta x_i = 0.05$  were selected. On the basis of the calculated temperatures of primary crystallization the liquidus surface equations of individual phases were calculated using the method of multiple linear regression analysis. From these equations the isotherms of primary crystallization for the chosen temperature step of 100 °C were calculated. The boundary lines were determined as cross-sections of two neighbouring liquidus surfaces with equal temperature of primary crystallization. The coordinates of the eutectic points were obtained as cross-sections of three boundary lines.

The calculation of the liquidus temperature of individual phases,  $T_{\text{liq}}(i)$ , was performed using the simplified and modified LeChatelier—Shreder equation [12]

$$T_{\text{liq}}(i) = \frac{\Delta_{\text{fus}}H(i)T_{\text{fus}}(i)}{\Delta_{\text{fus}}H(i) - RT_{\text{fus}}(i) \ln a(i)} \quad (14)$$

where  $T_{\text{fus}}(i)$  and  $\Delta_{\text{fus}}H(i)$  is the temperature and enthalpy of fusion of the  $i$ -th phase, respectively, and  $a(i)$  is its activity calculated according to the respective form of eqn (4). The first crystallizing phase at the given composition was determined according to the condition

$$T_{\text{pc}}(i) = \max_i (T_{\text{liq}}(i)) \quad (15)$$

The needed thermodynamic data, *i.e.* the temperatures and enthalpies of fusion of individual phases were taken from the literature and are summarized in Table 1. The experimentally determined phase diagrams of the systems CaO—TiO<sub>2</sub> and CaO—TiO<sub>2</sub>—SiO<sub>2</sub> were taken from the work of *De Vries et al.* [13].

## RESULTS AND DISCUSSION

a) System CaO—TiO<sub>2</sub>

The experimentally determined [13] and calculated phase diagrams of the system CaO—TiO<sub>2</sub> are shown in Figs. 1 and 2, respectively. The activities of individual phases, *i.e.* CaO, Ca<sub>3</sub>Ti<sub>2</sub>O<sub>7</sub>, CaTiO<sub>3</sub>, and TiO<sub>2</sub> were calculated using eqns (6), (10), (11), and (12), respectively.

As follows from the comparison of Figs. 1 and 2, the agreement between the calculated and experimental

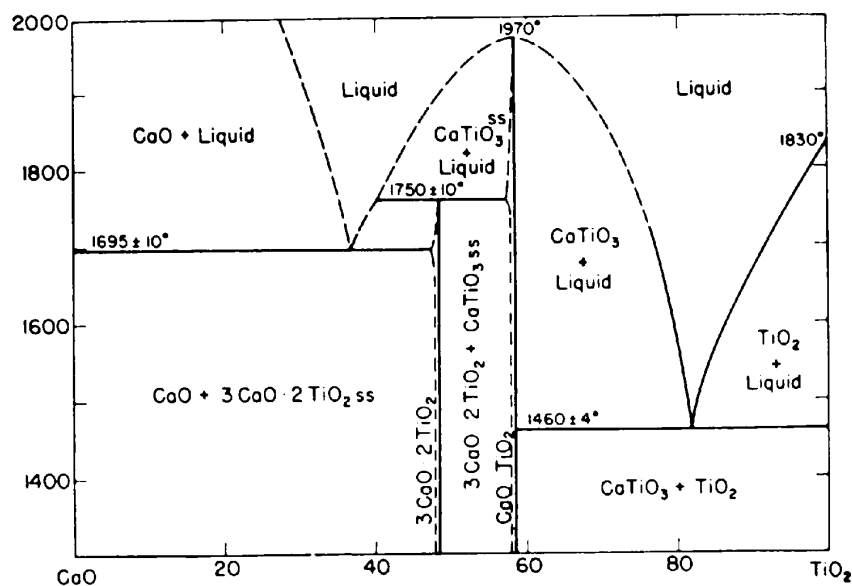


Fig. 1. Experimental phase diagram of the system CaO—TiO<sub>2</sub> according to [13].

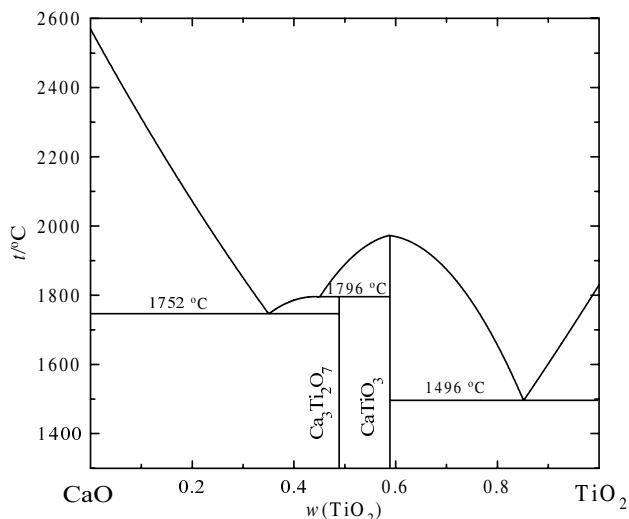
**Table 1.** Temperatures and Enthalpies of Fusion of Pure Substances Used in the Calculation

Compound	$T_{\text{fus}}$ K	$\Delta_{\text{fus}}H$ kJ mol <sup>-1</sup>	Ref.
CaO	2843	52.0	[14]
Ca <sub>2</sub> SiO <sub>4</sub>	2403	55.4	[14]
CaSiO <sub>3</sub>	1817	56.0	[14]
CaTiSiO <sub>5</sub>	1656	139.0	[15]
Ca <sub>3</sub> Ti <sub>2</sub> O <sub>7</sub>	≈ 2070*	265.0**	Estimated
CaTiO <sub>3</sub>	2243	127.3***	Estimated
TiO <sub>2</sub>	2103	66.9	[14]
SiO <sub>2</sub>	1986	9.6	[14]

\* $T_{\text{fus,hyp}}(\text{Ca}_3\text{Ti}_2\text{O}_7) \approx 2070$  K,  $\Delta_{\text{fus}}S(\text{atom}) \approx 10.7$  J mol<sup>-1</sup> K<sup>-1</sup>.

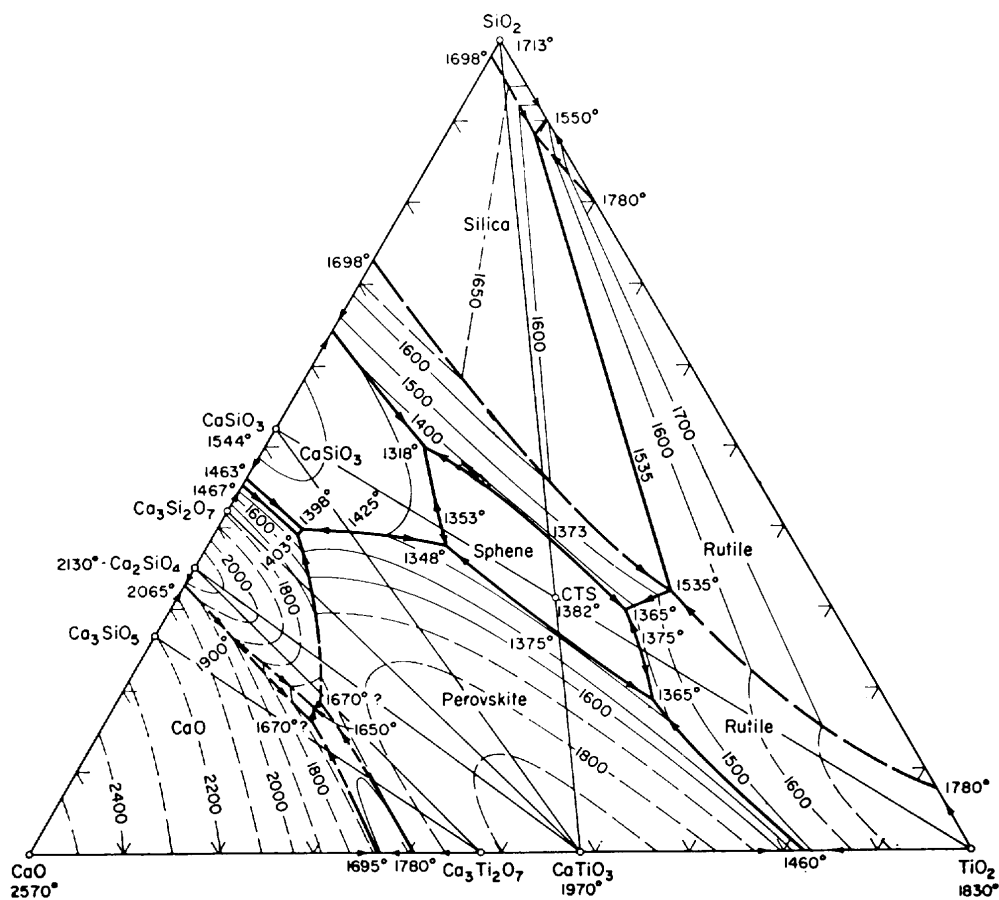
\*\* $\Delta_{\text{fus}}H(\text{Ca}_3\text{Ti}_2\text{O}_7) \approx 12 \times \Delta_{\text{fus}}S(\text{atom}) \times T_{\text{fus,hyp}}(\text{Ca}_3\text{Ti}_2\text{O}_7)$ .

\*\*\* $\Delta_{\text{fus}}H(\text{CaTiO}_3) \approx T_{\text{fus}}(\text{CaTiO}_3) \times \Delta_{\text{fus}}S(\text{MgTiO}_3)$ .

**Fig. 2.** Calculated phase diagram of the system CaO—TiO<sub>2</sub>.

phase diagram is very good. With regard to the relatively big difference between the temperature of fusion of CaTiO<sub>3</sub> and the adjacent eutectic temperatures the temperature dependence of the enthalpy of fusion of this compound has been taken into account introducing the heat capacity of fusion  $\Delta_{\text{fus}}C_p(\text{CaTiO}_3) = 250$

J mol<sup>-1</sup> K<sup>-1</sup>. Besides that, the liquidus curves of TiO<sub>2</sub> and SiO<sub>2</sub> were calculated under the assumption that  $a_i = x_i$ . The total deviation between the calculated and experimentally determined liquidus temperatures is 64°C.

**Fig. 3.** Experimental phase diagram of the system CaO—TiO<sub>2</sub>—SiO<sub>2</sub> according to [13].

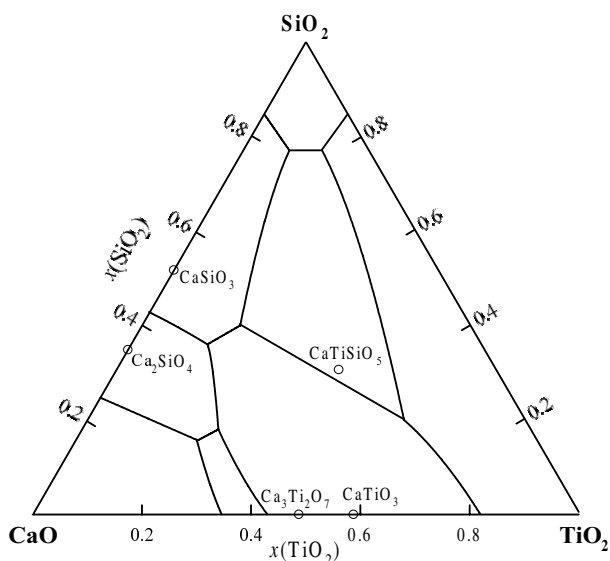


Fig. 4. Calculated phase diagram of the system CaO—TiO<sub>2</sub>—SiO<sub>2</sub>.

#### b) System CaO—TiO<sub>2</sub>—SiO<sub>2</sub>

The experimentally determined [13] and calculated phase diagram of the system CaO—TiO<sub>2</sub>—SiO<sub>2</sub> is shown in Figs. 3 and 4, respectively. Some existing phases in this ternary system, like the rankinite and tricalcium silicate, were not included into the calculation because of lack of relevant thermodynamic data.

The activities of individual phases, *i.e.* CaO, Ca<sub>2</sub>SiO<sub>4</sub>, CaSiO<sub>3</sub>, Ca<sub>3</sub>Ti<sub>2</sub>O<sub>7</sub>, CaTiO<sub>3</sub>, CaTiSiO<sub>5</sub>, TiO<sub>2</sub>, and SiO<sub>2</sub> were calculated using eqns (6) to (13). Besides the above-mentioned approach in the calculation of the liquidus surfaces of phases present in the CaO—TiO<sub>2</sub> boundary, the liquidus surface of CaSiO<sub>3</sub> was calculated under the assumption that there is the region of solid solutions in CaSiO<sub>3</sub> up to 30 mole % at the temperature of 1350 °C. The activity of Ca<sub>2</sub>SiO<sub>4</sub> in the basic region was calculated according to eqn (7a), while in the acidic region the Ca<sub>2</sub>SiO<sub>4</sub> activity was calculated according to eqn (7b).

In the region of high content of SiO<sub>2</sub> the calculation of the phase equilibrium fails since the formation of two liquids is not considered in the thermodynamic model of silicate melts. This is also the reason for the enlarged liquidus surface of CaTiSiO<sub>5</sub> up to the high content of silica.

### CONCLUSION

From the comparison of the calculated and experimental phase diagrams it follows that the thermodynamic model of silicate melts is suitable for describing

the phase equilibrium also in titanium-bearing silicate systems. The introduction of structural aspects into the thermodynamic model provides deeper information about the behaviour of individual components. Some disagreements in the case of some calculated and experimental phase diagrams are obviously caused by either inadequate structural assumptions or unreliable thermodynamic data. In our previous work [16], as well as in the present paper it was shown that TiO<sub>2</sub> behaves in the silicate melts as network-forming oxide, except in the region of its high concentration, and in highly basic melts.

*Acknowledgements.* The present work was financially supported by the Scientific Grant Agency VEGA of the Ministry of Education of the Slovak Republic and the Slovak Academy of Sciences under the Grant No. 2/5119/98.

### REFERENCES

1. Mysen, B. and Neuville, D., *Geochim. Cosmochim. Acta* 59, 325 (1995).
2. Lange, R. A. and Navrotsky, A., *Geochim. Cosmochim. Acta* 57, 3001 (1993).
3. Schneider, E., Wong, J., and Thomas, J. M., *J. Non-Cryst. Solids* 136, 1 (1991).
4. Liška, M., Hulínová, H., Šimurka, P., and Antalík, J., *Ceramics-Silikáty* 39, 20 (1995).
5. Richet, P. and Bottinga, Y., *Geochim. Cosmochim. Acta* 49, 471 (1985).
6. Pelton, A. D., *Thermodynamically Optimized Phase Diagrams of Oxide Systems*. Final Report, Centre de Recherche en Calcul Thermochimique, Ecole Polytechnique, Montreal, Canada, 1994.
7. Kohler, F., *Monatsh. Chem.* 91, 738 (1960).
8. DeCapitani, C. and Kirschen, M., *Geochim. Cosmochim. Acta* 62, 3753 (1998).
9. Kirschen, M. and DeCapitani, C., MinPet96, Gemeinschaftstagung SMPG, ÖMG, Schwaz, Österreich, 1996.
10. Pánek, Z. and Daněk, V., *Silikáty* 21, 97 (1977).
11. Liška, M. and Daněk, V., *Ceramics-Silikáty* 34, 215 (1990).
12. Malinovský, M. and Roušar, I., *Termodynamické základy anorganických pochodov.* (Thermodynamic Fundamentals of Inorganic Processes.) Nakladatelství technické literatury (Publishers of the Technical Literature), Prague, 1982.
13. De Vries, R. C., Roy, R., and Osborn, E. F. J., *J. Am. Ceram. Soc.* 38, 158 (1955).
14. Barin, I. and Knacke, O., *Thermochemical Properties of Inorganic Substances*. Springer-Verlag, Berlin, 1973.
15. Nerád, I., Kosa, L., Mikšíková, E., Šaušová, S., and Adamkovičová, K., *Proceedings of the Sixth International Conference on Molten Slags, Fluxes and Salts*. Stockholm, Sweden—Helsinki, Finland, 12—17 June, 2000. ISBN 91-7170-606-2, Trita Met 85 June 2000, CD ROM.
16. Nerád, I. and Daněk, V., *Chem. Pap.* 56, 77 (2002).