

# Thermodynamic Modeling of the CaO-SiO<sub>2</sub>-M<sub>2</sub>O (M=K,Na) systems

Ligang Zhang<sup>1\*</sup>, Clemens Schmetterer<sup>1</sup>, Patrick J. Masse<sup>2</sup>

<sup>1</sup>Freiberg University of Mining and Technology, Centre for Innovation Competence VIRTUHCON, Research Group “Multiphase Systems”, Fuchsmühlenweg 9, Reiche Zeche, 09596 Freiberg, Germany

<sup>2</sup>ATZ Entwicklungszentrum, An der Maxhütte 1, D-92237 Sulzbach-Rosenberg, Germany

**Abstract:** The aim of the present study is the CALPHAD modeling of the systems CaO-SiO<sub>2</sub>-M<sub>2</sub>O (M=K, Na) based on a careful review of the available literature data – phase diagram and thermodynamics – as well as own experiments. The heat capacities (C<sub>p</sub>) of three compounds, CaSiO<sub>3</sub>, K<sub>2</sub>Ca<sub>2</sub>Si<sub>2</sub>O<sub>7</sub> and K<sub>8</sub>CaSi<sub>10</sub>O<sub>25</sub>, (determined using drop calorimetry) were included in the optimization of the ternary phase diagram CaO-SiO<sub>2</sub>-K<sub>2</sub>O.

**Key words:** Thermodynamics, Phase diagram, Modeling, Molten slag

## 1. Introduction

The aim of the Virtual High temperature Conversion Processes (VIRTUHCON) project is the theoretical modeling of high temperature conversion processes such as metallurgy and gasification. The thermodynamic properties of molten silicates (slag) are important input quantities for the modeling of phenomena in process engineering and geoscience where SiO<sub>2</sub> (silica) is a prime component. Although the alkaline oxides normally appear in minor quantities, they can significantly change the behavior of the slag properties because of their low melting temperatures thereby considerably lowering the liquidus temperature of the molten oxide mixture. Therefore, information on phase diagram and thermochemistry of alkaline oxide containing systems is required to help scientists in the design or development of new materials and processes. However, experimental difficulties abound in alkaline bearing systems because SiO<sub>2</sub> is volatile at high temperatures and alkaline oxides are difficult to handle and prone to surface hydrolysis when exposed to air. CALPHAD modeling is therefore considered a suitable choice to provide phase diagram and thermochemical information where experiments can only be performed with difficulty.

The phase diagram and thermochemical information of the K<sub>2</sub>O-SiO<sub>2</sub> and Na<sub>2</sub>O-SiO<sub>2</sub> systems have already been thermodynamically evaluated in the literature [1-7]. There, the liquid phase was described using the modified quasi-chemical model [8] and the modified associate species model [9]. In the present work, the ionic two-sublattice model [10-11] is applied to describe the liquid phase in these systems as this model allows an adequate representation of the thermodynamic properties for complex liquids such as slag. Furthermore, this model allows coupling a large database for oxides to simple metal systems. A detailed literature review of these two systems can be found in Ref. [11], while new assessments of the K<sub>2</sub>O-SiO<sub>2</sub> and Na<sub>2</sub>O-SiO<sub>2</sub> systems were recently carried out by Schmetterer et al. and Zhang et al. [12, 13].

The thermodynamic parameters of the CaO-SiO<sub>2</sub> system have been optimized several times [14-17]. Recently, we performed a survey of literature data for the C<sub>p</sub> of the calciumsilicate phases [18] and made a new determination of the

Cp of Pseudowollastonite ( $\text{CaSiO}_3$  – see Table 1) which was found to be in good agreement with the literature. These results were included in our thermodynamic description of this system.

However, no phase diagram and thermochemical information for the  $\text{K}_2\text{O}$ -CaO and  $\text{Na}_2\text{O}$ -CaO systems are available so that the thermodynamic descriptions of these two systems had to be based on simple extrapolations of the Gibbs energy functions of the pure oxides compounds.

Literature for the ternary systems is scarce; the key papers for experimental investigations are from Morey et al. [19] for the  $\text{K}_2\text{O}$ -CaO- $\text{SiO}_2$  system and Morey and Bowen [20] for the  $\text{Na}_2\text{O}$ -CaO- $\text{SiO}_2$ . In their reports the authors provided liquidus temperatures obtained from optical inspection of samples after quenching from various temperatures and reported the existence and composition of several ternary compounds. However, the experiments were mostly confined to the  $\text{SiO}_2$  rich part. Six ternary compounds in this CaO- $\text{K}_2\text{O}$ - $\text{SiO}_2$  system,  $\text{CaK}_2\text{SiO}_4$ ,  $\text{CaK}_4\text{Si}_3\text{O}_9$ ,  $\text{CaK}_8\text{Si}_{10}\text{O}_{25}$ ,  $\text{Ca}_3\text{K}_2\text{Si}_6\text{O}_{16}$ ,  $\text{Ca}_2\text{K}_2\text{Si}_6\text{O}_{15}$  and  $\text{Ca}_2\text{K}_2\text{Si}_9\text{O}_{21}$  were reported by Morey et al. [19]. However, they did not give any structural information in their work. Toropov and Borisenko [21] and Yung et al. [22] indicted the existence of the compound  $\text{CaK}_4\text{Si}_6\text{O}_{15}$  based on X-Ray studies. Recently, the possible existence of  $\text{CaK}_2\text{SiO}_4$  was checked [23], but the evaluations of the powder diffractograms obtained after synthesis experiments clearly indicated that for a 1:1:1 bulk composition  $\text{K}_2\text{Ca}_2\text{Si}_2\text{O}_7$  is the dominant potassium calcium silicate up to the melt formation. There is no thermochemical information available in this ternary system. The CaO- $\text{Na}_2\text{O}$ - $\text{SiO}_2$  system had been studied first by Morey and Bowen [20] who mentioned the existence of four ternary compounds  $\text{Ca}_3\text{Na}_2\text{Si}_6\text{O}_{16}$ ,  $\text{Ca}_2\text{Na}_2\text{Si}_3\text{O}_9$ ,  $\text{CaNa}_4\text{Si}_3\text{O}_9$ , and  $\text{CaNa}_2\text{SiO}_4$ . Segnit [24] had obtained the new compound  $\text{Ca}_3\text{Na}_8\text{Si}_5\text{O}_{17}$  and  $\text{Ca}_2\text{Na}_2\text{Si}_2\text{O}_7$  in the parts of this ternary system richer in CaO and  $\text{Na}_2\text{O}$ . The compound  $\text{Ca}_8\text{Na}_4\text{Si}_5\text{O}_{20}$  had been found by Toropov and Arakelyan [25]. Later, Fedorov and Brodkina [26] considered this phase to be a mixture of a solid solution with  $\text{Ca}_2\text{SiO}_4$  and  $\text{CaNa}_2\text{SiO}_4$  instead of an individual compound. The six ternary compounds from the literature were considered in this work. The phase diagram and thermochemical information is also limited in this ternary system to the work from Morey and Bowen [20]. Further experimental phase diagram data and thermodynamic properties have not been determined until now.

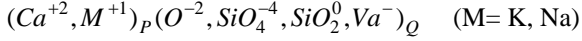
The goal of the present work is to describe the current knowledge about the thermodynamic properties of the  $\text{M}_2\text{O}$ -CaO- $\text{SiO}_2$  ( $\text{M}=\text{K}, \text{Na}$ ) ternary systems which are constituents of the complex  $\text{Al}_2\text{O}_3$ -CaO-MgO- $\text{SiO}_2$ - $\text{M}_2\text{O}$  ( $\text{M}=\text{K}, \text{Na}$ ) system. The optimization of these ternary systems is the first step in the estimation of thermodynamic properties and phase diagrams of the subsequent multicomponent systems.

## 2. Thermodynamic Modeling

### 2.1 Liquid phase

It can be assumed that  $\text{Ca}^{2+}$ ,  $\text{K}^+$ ,  $\text{Na}^+$ ,  $\text{O}^{2-}$ ,  $\text{SiO}_4^{4-}$ ,  $\text{SiO}_2^0$  and  $\text{Va}^-$  exist in the liquid phase of the CaO- $\text{M}_2\text{O}$ - $\text{SiO}_2$  ( $\text{M}=\text{K}, \text{Na}$ ) systems, and that the electric neutrality is maintained depending on the relative amounts of positive or negative ions for a given temperature. The two-sublattice model for the ionic solution suggested by Hillert et al. [10] can be used to express the Gibbs energy of this system. This model utilizes two sublattices, one for cations and the other for anions,

neutral species and vacancies. Thus, the formula unit of the CaO-M<sub>2</sub>O-SiO<sub>2</sub> (M=K, Na) systems can be expressed as



where  $Va^-$  denotes the vacancies. The indices P and Q represent the mole number of cations and anions of the two sublattices in order to maintain the electric neutrality, as described by Eqs. (1) and (2)

$$P = 2y_{O^{-2}} + 4y_{SiO_4^{-4}} \quad (1)$$

$$Q = y_{M^{+1}} + 2y_{Ca^{+2}} \quad (2)$$

Although this model yields complicated thermodynamic expressions, in practice, all calculations are carried out automatically using thermodynamic software packages such as Thermo-Calc [27]. The Gibbs energy of the liquid in this system is given by Eq. (3)

$$G_m = \sum \sum y_i y_j {}^0G_{ij} + Q \sum y_k {}^0G_k + PRT \sum y_i \ln y_i + QRT (\sum y_j \ln y_j + \sum y_k \ln y_k) + {}^E G_m \quad (3)$$

where  $i$  is a cation,  $Ca^{+2}$  or  $K^{+1}$  or  $Na^{+1}$ ,  $j$  is an anion,  $O^{-2}$  or  $SiO_4^{-4}$ , and  $k$  is neutral as in

$SiO_2^0$ ,  ${}^E G_m$  represents excess Gibbs energy. The last term,  ${}^E G_m$ , can be expressed by Eq. (4)

$${}^E G_m = \sum_{v=0}^{v=s} y_i y_j y_k \sum_{v=0}^{v=n} {}^v L_{i,j,k} (y_j - y_k)^v + \sum_{v=0}^{v=n} y_i y_j y_k y_l L_{i,j,k,l} (y_i - y_j)(y_k - y_l) \quad (4)$$

where  $i, j, k$  and  $l$  is a cation or anion or neutral as in  $SiO_2^0$ .  $L_{i,j,k}$  and  $L_{i,j,k,l}$  are the interaction parameters between two sub-lattices that were optimized in this work.

## 2.2 Solid phases

In the CALPHAD technique, the thermodynamic properties of each solid phase are represented by the parameters  $S_{298}$  (the entropy of the solid at 298.15 K),  $C_p(T)$  (the heat capacity of the solid) and  $\Delta H_{298}$ , (the change in enthalpy of the solid) where

$$C_p = a + bT + cT^{-2} \quad (5)$$

The Gibbs energy values are given in relation to the enthalpy of selected reference states for the elements at 298.15 K according to Eq. (6). This state is denoted by SER (Stable Element Reference)

$${}^0G - H^{SER} = A + B/T + CT + DT \ln T + ET^2 + \dots \quad (6)$$

with the parameters  $A, B, C, D$  and  $E$  being optimized, i.e. determined in such a way that the calculated phase diagram matches the experimental information.

In the current work, the Gibbs functions of three compounds  $K_2Ca_2Si_2O_7$  and  $K_8CaSi_{10}O_{25}$  were based on our own

heat capacity data from drop calorimetry [28]. The thermodynamic parameters of other compounds were assessed based on the phase relations from the work of Morey et al. [19]. So far, the interpretation of the results concerning the existence and formation of certain phases had to rely exclusively on the only available phase equilibrium study of the  $K_2O$ - $CaO$ - $SiO_2$  ternary system that was published 80 years ago by Morey et al. [19]. The optimization of the  $CaO$ - $M_2O$ - $SiO_2$  ( $M=K, Na$ ) systems was carried out using the Thermo-Calc software [27]. This module works by minimizing the square sum of the differences between experimental and calculated values. In the optimization procedure, each set of experimental data was given a certain weight. The weights were changed systematically during the optimization until most of the experimental data could be accounted for within the claimed uncertainty limits.

The parameters for the liquid phase were first optimized using the experimental liquidus temperatures. The thermodynamic parameters of the solid compounds were assessed next by using the phase diagram data and the heat capacities. All of the parameters were finally evaluated together to give a reasonable description of these systems.

The thermodynamic parameters from the optimization are listed in Table 1 below.

Table 1 Thermodynamic parameters of  $CaO$ - $SiO_2$ - $M_2O$  ( $M=K, Na$ ) systems

Phase	Thermodynamic Parameters (J/mol)
$Ca_2K_2Si_2O_7$	$G_{Ca_2K_2Si_2O_7} = -4 \times 10^6 + 1878.85T - 296.52202T \ln T - 0.0213315T^2 + 1447659.99T^{-1}$
$CaK_4Si_3O_9$	$G_{CaK_4Si_3O_9} = -3.73 \times 10^5 + 10T + 2GK_2O + 3GSiO_2 + GCAO$
$CaK_8Si_{10}O_{25}$	$G_{Ca_2K_2Si_2O_7} = -5733236.456 + 1475.356T - 1049T \ln T - 9.6487 \times 10^6 T^{-1}$
$CaK_4Si_6O_{15}$	$G_{CaK_4Si_6O_{15}} = -3.93 \times 10^5 + 9.005T + 2GK_2O + 6GSiO_2 + GCAO$
$Ca_3K_2Si_6O_{16}$	$G_{Ca_3K_2Si_6O_{16}} = -4.65 \times 10^5 + 8.04T + GK_2O + 6GSiO_2 + 3GCAO$
$Ca_2K_2Si_6O_{15}$	$G_{Ca_2K_2Si_6O_{15}} = -3.704 \times 10^5 + 10.01T + GK_2O + 6GSiO_2 + 2GCAO$
$Ca_2K_2Si_9O_{21}$	$G_{Ca_2K_2Si_9O_{21}} = -3.72 \times 10^5 + 10.01T + GK_2O + 9GSiO_2 + 2GCAO$
$CaNa_2SiO_4$	$G_{CaNa_2SiO_4} = -2.2015 \times 10^5 + 48.85T + GNA_2O + GSiO_2 + GCAO$
$Ca_3Na_8Si_5O_{17}$	$G_{Ca_3Na_8Si_5O_{17}} = -4.93015 \times 10^5 + 70.0025T + 4GNA_2O + 5GSiO_2 + 3GCAO$
$Ca_2Na_2Si_2O_7$	$G_{Ca_2Na_2Si_2O_7} = -3.40009 \times 10^5 + 64.0018T + GNA_2O + 2GSiO_2 + 2GCAO$
$Ca_2Na_2Si_3O_9$	$G_{Ca_2Na_2Si_3O_9} = -3.98009 \times 10^5 + 70.0018T + GNA_2O + 3GSiO_2 + 2GCAO$
$CaNa_4Si_3O_9$	$G_{CaNa_4Si_3O_9} = -4.54 \times 10^5 + 108.037T + 2GNA_2O + 3GSiO_2 + GCAO$
$Ca_3Na_2Si_6O_{16}$	$G_{Ca_3Na_2Si_6O_{16}} = -4.904 \times 10^5 + 70T + GNA_2O + 6GSiO_2 + 3GCAO$

### 3. Results and Discussions

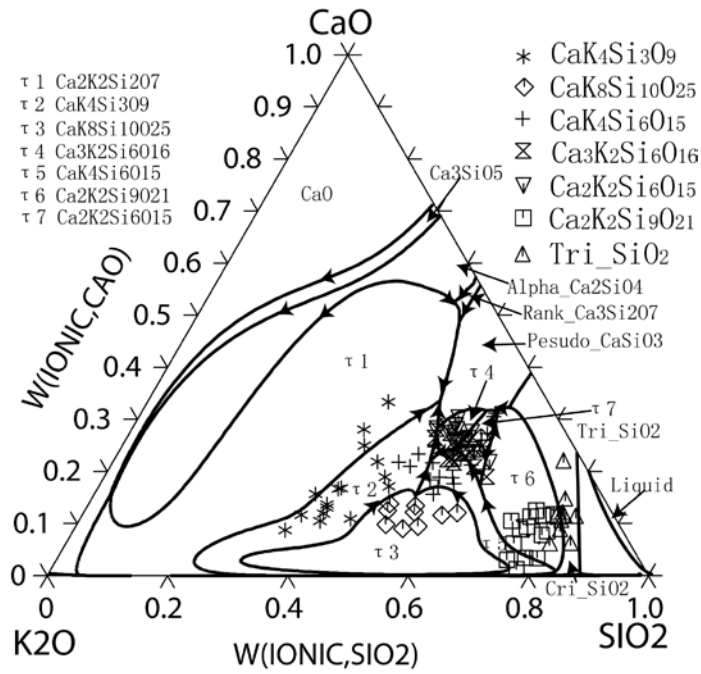


Fig. 1 Calculated phase diagram of CaO-K<sub>2</sub>O-SiO<sub>2</sub> system

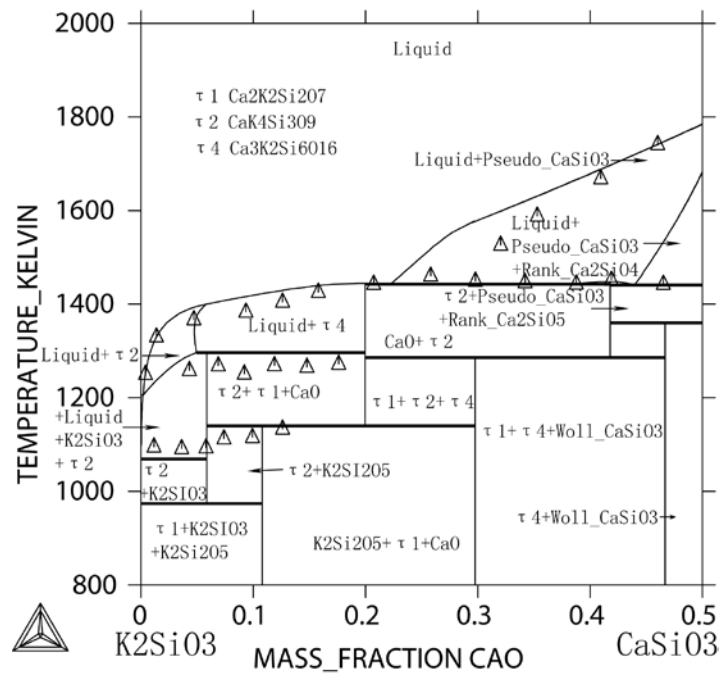


Fig. 2 Calculated vertical section (K<sub>2</sub>SiO<sub>3</sub>-CaSiO<sub>3</sub>) with experimental results [19]

Seven ternary compounds were included in the CaO-K<sub>2</sub>O-SiO<sub>2</sub> system. The Cp data from our own measurement for

the compounds  $K_2Ca_2Si_2O_7$  and  $K_8CaSi_{10}O_{25}$  were considered in this optimization. The calculated liquidus temperatures are shown in Fig. 1, which is in good agreement with the experimental results from Morey et al. [19] in the respective composition range. It has, however, to be noted that the  $K_2O$ -rich part is extrapolated and not supported by experimental data. Comparing our calculated results with the experimental results, it can be found that there are differences between the experimental data [19] and the calculated results close to the compound  $CaK_4Si_6O_{15}$ . This region still needs experimental attention and further optimization.

A calculated vertical section ( $K_2SiO_3$ - $CaSiO_3$ ) of the  $CaO$ - $K_2O$ - $SiO_2$  ternary system is given in Fig. 2. Again it can be seen that the agreement between the present calculation and the measurement is good. The calculated liquidus surface of the  $CaO$ - $Na_2O$ - $SiO_2$  system is shown in Fig. 3 together with the primary crystallization fields. The six ternary compounds reported in the literature were included in the calculation. Figure 4 shows the calculated isothermal section at 2000 K, where the liquid miscibility gap close to the  $SiO_2$  corner extends into the ternary system. With increasing temperature the boundary of the miscibility gap will shift toward the  $CaO$ - $SiO_2$  binary system. The calculated invariant reactions on this system were shown in Table 3. The isothermal section at 1273 K is given in Fig. 5, where five ternary compounds,  $Ca_2Na_2Si_2O_7$ ,  $CaNa_2SiO_4$ ,  $Ca_2Na_2Si_3O_9$ ,  $CaNa_4Si_4O_9$ ,  $Ca_3Na_2Si_6O_{16}$ , are stable. The calculated vertical section ( $Na_2SiO_4$ - $CaSiO_3$ ) of this ternary system is given in Fig. 6 and shows good agreement between the present calculation and the measurements [20].

Table 3 Invariant reactions of  $CaO$ - $SiO_2$ - $M_2O$  ( $M=K, Na$ ) systems

Reaction	Type	T/K	Ref
$L+Ca_2K_2Si_2O_7 \rightleftharpoons \text{Pesudo\_}CaSiO_3+CaK_4Si_3O_9$	U	1073	[19]
		1061	This work
		1050	[19]
$L \rightleftharpoons \text{Pesudo\_}CaSiO_3+CaK_4Si_3O_9+Ca_3K_2Si_6O_{16}$	E	1049	This work
		1273	[19]
$L+\text{Pesudo\_}CaSiO_3+Ca_2K_2Si_6O_{15} \rightleftharpoons Ca_3K_2Si_6O_{16}$	P	1257	This work
		1170	[19]
$L+CaK_8Si_{10}O_{25} \rightleftharpoons CaK_4Si_3O_9+CaK_4Si_6O_{15}$	U	1157	This work
		1098	[19]
$L+Ca_2K_2Si_9O_{21} \rightleftharpoons Ca_2K_2Si_6O_{15}+CaK_4Si_6O_{15}$	U	1065	This work
		1223	[19]
$L+Ca_2K_2Si_6O_{15} \rightleftharpoons Ca_3K_2Si_6O_{16}+CaK_4Si_6O_{15}$	U	1234	This work
		1323	[20]
$L+\text{Pesudo\_}CaSiO_3 \rightleftharpoons Ca_3Na_2Si_6O_{16}+Tri\_SiO_2$	U	1354	This work
		1423	[20]
$L+Ca_2Na_2Si_2O_7 \rightleftharpoons Ca_3Na_2Si_6O_{16}+Ca_2Na_2Si_3O_9$	U	1417	This work
		1157	[20]
$L+Ca_3Na_2Si_6O_{16}+Ca_2Na_2Si_3O_9 \rightleftharpoons CaNa_4Si_3O_9$	P	1170	This work

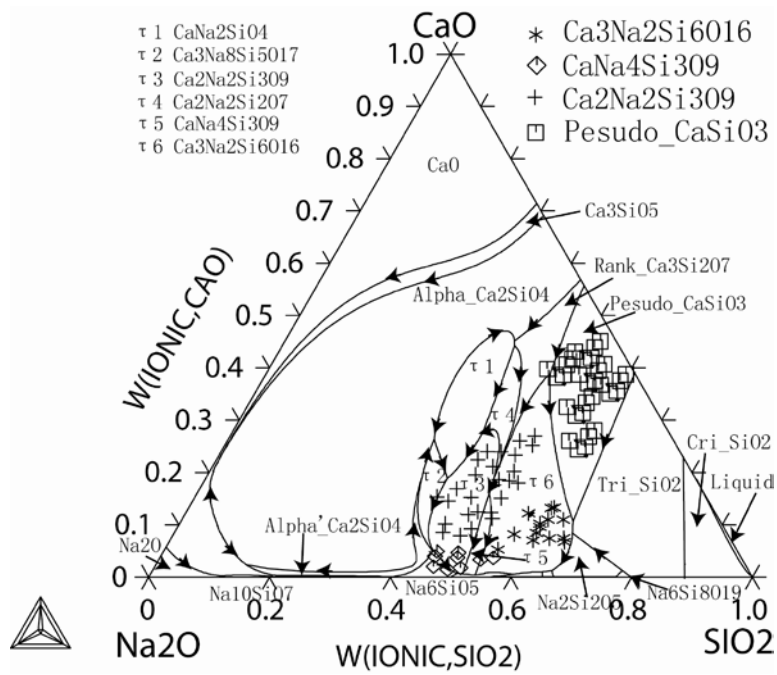


Fig. 3 Calculated phase diagram of CaO-Na<sub>2</sub>O-SiO<sub>2</sub> system

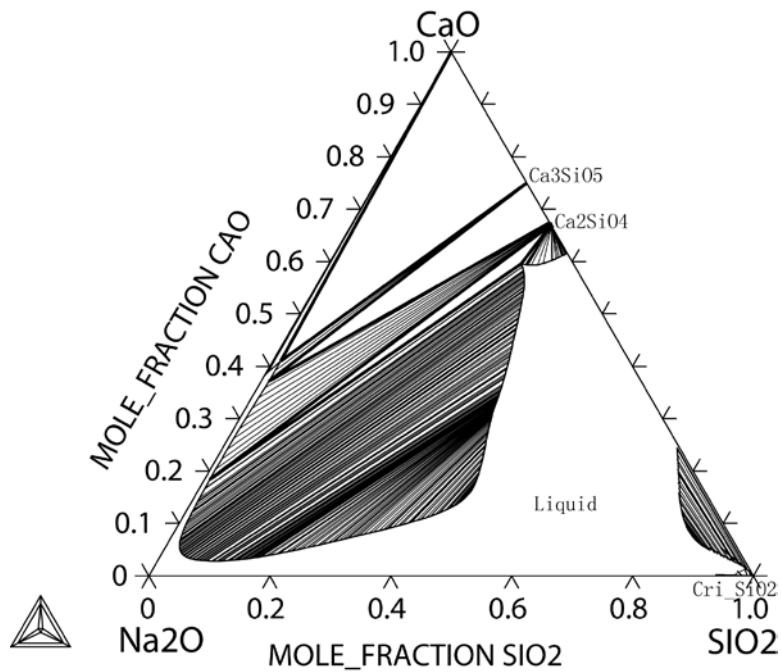


Fig. 4 Calculated isothermal section at 2000 K in CaO-Na<sub>2</sub>O-SiO<sub>2</sub> system

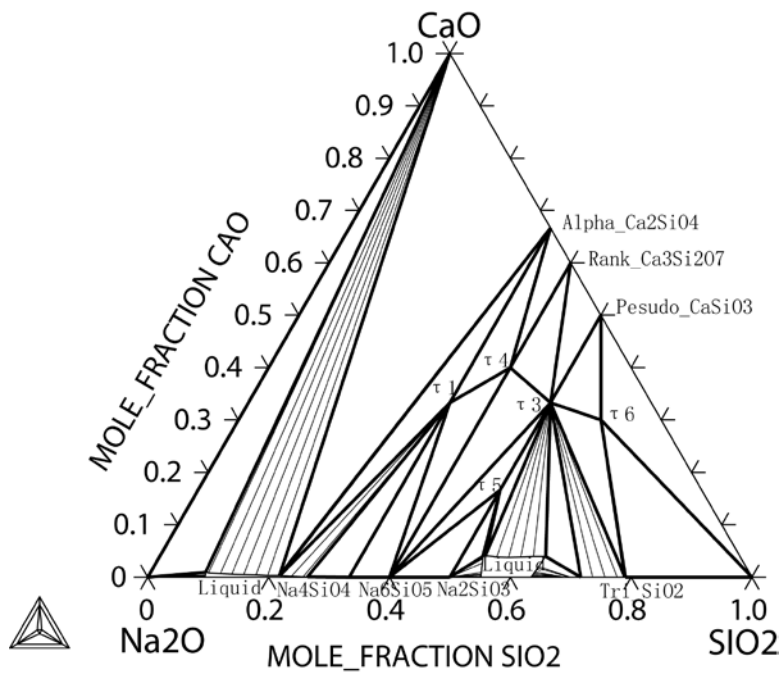


Fig. 5 Calculated isothermal section at 1273 K

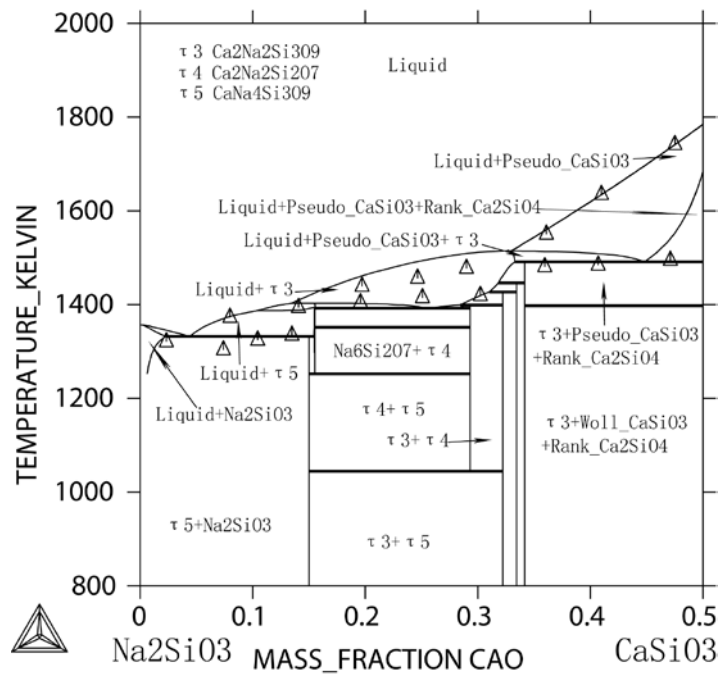


Fig. 6 Calculated vertical section ( $\text{Na}_2\text{SiO}_3$ - $\text{CaSiO}_3$ )



#### 4. Conclusions

Based on the previous assessments and our own optimization of the sub-binary systems, the thermodynamic properties and phase equilibria of the  $\text{CaO-M}_2\text{O-SiO}_2$  ( $\text{M}=\text{K, Na}$ ) systems have been assessed. The two-sublattice model for ionic solutions can be used to describe these two ternary systems. In addition, the experimentally determined heat capacities of three solid compounds were included in the dataset. Reasonable agreement between calculated and experimental data has been achieved.

Nevertheless, the need of more experimental information for the phase diagrams and thermodynamic properties is desirable in order to have more detailed and confident phase diagram description. Experimental work in the  $\text{CaO-M}_2\text{O-SiO}_2$  ( $\text{M}=\text{K, Na}$ ) systems is therefore strongly encouraged.

#### Acknowledgement

This research has been funded by the Federal Ministry of Education and Research of Germany in the framework of Virtuhcon (project number 03z2FN12).

#### References

- [1] P. Wu, G. Eriksson, A.D. Pelton. Optimization of the thermodynamic properties and phase diagrams of the  $\text{Na}_2\text{O-SiO}_2$  and  $\text{K}_2\text{O-SiO}_2$  systems. *J. Am. Ceram. Soc.*, 1993, 76, p2059-2064
- [2] A.D. Pelton, P. Wu. Thermodynamic modeling in glass-forming melts. *J. Non-Crystalline Solids*, 1999, 253, p178-191
- [3] S. Forsberg. Optimization of thermodynamic properties of the  $\text{K}_2\text{O-SiO}_2$  system at high temperatures. *J. Phase Equilibria*, 2002, 23, p211-217
- [4] S.S. Kim, T.H. Sanders. Thermodynamic modeling of phase diagrams in binary alkali silicate systems. *J. Am. Ceram. Soc.*, 1991, 74, p1833-1840
- [5] E. Yazhenskikh, K. Hack, M. Muller. Critical thermodynamic evaluation of oxide systems relevant to fuel ashes and slags. Part 1: Alkali oxide-silica systems. *CALPHAD*, 2006, 30, p270-276
- [6] A. Romero-Serrano, C. Gomez-Yanez, M. Hallen-Lopez, J. Araujo-Osorio. Thermodynamic Modeling of Alkali Metal Oxide - Silica Binary Melts. *J. Am. Ceram. Soc.*, 2005, 88, p141-145
- [7] G. Lambotte, P. Chartrand. Thermodynamic optimization of the  $(\text{Na}_2\text{O}+\text{SiO}_2+\text{NaF}+\text{SiF}_4)$  reciprocal system using the Modified Quasichemical Model in the Quadruplet Approximation. *J. Chemical Thermodynamics*, 2011, 43, p1678-1699
- [8] A.D. Pelton, M. Blander. Thermodynamic analysis of ordered liquid solutions by a modified quasichemical approach—application to silicate slags. *Metall. Trans. B*, 1986, 17B, p805-815
- [9] T.M. Besmann, K.E. Spear. Thermochemical modeling of oxide glasses. *J. Am. Ceram. Soc.*, 2002, 85, p2887-2894
- [10] M. Hillert, B. Jansson, B. Sundman, J. Agren. A two-sublattice model for molten solutions with different tendency for ionization. *Metall. Trans. A*, 1985, 16A, p261-266
- [11] B. Sundman. Modification of the two-sublattice model for liquids. *CALPHAD*, 1991, 15, p153-190
- [12] C. Schmetterer, L. Zhang, P. Masset. Thermodynamics of Alkaline Oxide Containing Slags. *Virtuhcon Newsletter*, 09/2011, p11-12 ([http://tu-freiberg.de/fakult4/iec/virtuhcon/VTC\\_downloads/newsletter\\_sept\\_2011.pdf](http://tu-freiberg.de/fakult4/iec/virtuhcon/VTC_downloads/newsletter_sept_2011.pdf))
- [13] L. Zhang, C. Schmetterer, P. J. Masset. Thermodynamic description of the  $\text{M}_2\text{O-SiO}_2$  ( $\text{M}=\text{K,Na}$ ) systems,

Computational Materials Science, submitted, 2012

- [14] J.R. Taylor, A.T. Dinsdale. Thermodynamic and phase diagram data for the CaO-SiO<sub>2</sub> system. CALPHAD, 1990, 14, p71-88
- [15] S. S. Kim, T. H. Sanders. Thermodynamic Modeling of the Miscibility Gaps and the Metastable Liquids in the MgO-SiO<sub>2</sub>, CaO-SiO<sub>2</sub>, and SrO-SiO<sub>2</sub> Systems. J. Am. Ceram. Soc., 1999, 82, p1901-1907
- [16] M. Hillert, Bo Sundman, X. Wang, T. Barry. A reevaluation of the rankinite phase in the CaO-SiO<sub>2</sub> system. CALPHAD, 1991, 15, p53-58
- [17] G. Eriksson, P. Wu, M. Blander, A.D. Pelton. Critical Evaluation and Optimization of the Thermodynamic Properties and Phase Diagrams of the MnO-SiO<sub>2</sub> and CaO-SiO<sub>2</sub> Systems. Canadian Metallurgical Quarterly, 1994, 33, p13-21
- [18] C. Schmetterer, P. J. Masset. Heat capacity of compounds in the CaO-SiO<sub>2</sub> system - a review, in preparation, 2012
- [19] G.W. Morey, F.C. Kracek, N.L. Bowen. The ternary system K<sub>2</sub>O-CaO-SiO<sub>2</sub>, J. Soc. Glass Techn., 1930, 14, p149-155
- [20] G. Morey, N. Bowen. The ternary system sodium metasilicate-calcium metasilicate-silica. J. Soc. Glass Techn., 1925, 9, p226-234
- [21] N.A. Toropov, A.I. Borisenko. Hydrated calcium silicates, Tsement, 1950, 5, p16-20
- [22] V.N. Yung, Y.M. Butt, V.V. Myshlyayev. Ibid., 1951, 6, p6-10
- [23] E. Arroyabe, R. Tessadri, D.M. Tobbens, V. Kahlenberg. Does K<sub>2</sub>CaSiO<sub>4</sub> exist? A phase-analytical study in the system K<sub>2</sub>O-CaO-SiO<sub>2</sub> with implications for the characterization of residual materials. J. Am. Ceram. Soc. 2011, 94, p2652-2655
- [24] E.R. Segnit. Further data on the system Na<sub>2</sub>O-CaO-SiO<sub>2</sub>. Amer. J. Sci., 1953, 251, p586-590
- [25] N.A. Toropov, O.I. Arakelyan. Chemistry of silicon and physical chemistry of silicates. DAN SSSR, 1950, 72, p356-359
- [26] N.F. Fedorov, E.R. Brodskina. Solid solutions in the system 2CaO.SiO<sub>2</sub>- K<sub>2</sub>O.CaO.SiO<sub>2</sub>. Izv. AN SSSR, Neorg. Mater., 1967, 3, p1283-1284
- [27] B. Sundman, B. Jansson, J.O. Andersson. The thermo-calc databank system. CALPHAD, 1985, 9, p153-190
- [28] C. Schmetterer, P. Vanek, V. Kahlenberg, P.J. Masset. Determination of the heat capacities of compounds in the K<sub>2</sub>O-CaO-SiO<sub>2</sub> system. Work in progress, 2012