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Immiscible silicate liquids in the system $\text{SiO}_2\text{-TiO}_2\text{-Al}_2\text{O}_3$

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Abstract: Coexisting liquids in the $\text{SiO}_2\text{-TiO}_2\text{-Al}_2\text{O}_3$ system have been synthesized at 2000 K to 2500 K with a laser-heated air levitation set-up in order to determine the $\text{SiO}_2\text{-TiO}_2$ miscibility gap and its extrapolation to the Al_2O_3 -bearing system. Compositions of quenched coexisting liquids in the $\text{SiO}_2\text{-TiO}_2$ and $\text{SiO}_2\text{-TiO}_2\text{-Al}_2\text{O}_3$ system demonstrate the dramatic decline of the miscibility gap when as little as 3 mol% Al_2O_3 is added. With bulk compositions containing 10 mol% Al_2O_3 we found no evidence of a stable liquid-liquid phase separation above 2073 K. While experimental liquidus data in the three binary subsystems can be modelled with Margules-type excess polynomials for the melt, the calculated ternary miscibility gap is strongly discrepant with experiments when conventional extrapolation methods are applied. To overcome this problem we propose a generalized extrapolation method based on weighting of the binary excess polynomials. Applying this multicomponent excess function an additional ternary excess term is not required and the experimentally determined liquid miscibility gap is reproduced in detail. Extrapolation outside the immiscibility region yields a valuable first-order approximation of the excess Gibbs free energy of the melt.

Key-words: liquid immiscibility, $\text{SiO}_2\text{-TiO}_2\text{-Al}_2\text{O}_3$ system, multicomponent excess function, linear programming.

Introduction

In order to compute phase-equilibrium diagrams in multicomponent silicate systems a solution model of the melt is required defining the activities of the end-members at given pressure, temperature and composition. Thus phase-equilibrium data are reduced to thermochemical databases and provide a valuable first-order approximation of phase relations when extrapolated outside the temperature and composition range of the experiments. Various methods have been applied in geological and ceramic literature to

model the excess Gibbs free energy of the melt in ternary and higher-order systems (e.g. Berman & Brown, 1984; Blander & Pelton, 1987; Schlesinger & Lynch, 1988; Huang *et al.*, 1994; Ghiorso & Sack, 1995; Hallstedt 1995). Recently, DeCapitani & Kirschen (1999) proposed a weighted extrapolation of binary Margules excess parameters W and modelled the excess Gibbs free energy of the melt in the ternary $\text{CaO-SiO}_2\text{-TiO}_2$ system without additional ternary parameter:

$$G^{xs} = \sum_{bin.} x_1 x_2 [W_{112} x_1 + W_{122} x_2] (x_1 + x_2)^{-t} \quad (1)$$

where x_i are mole fractions of the end-members of

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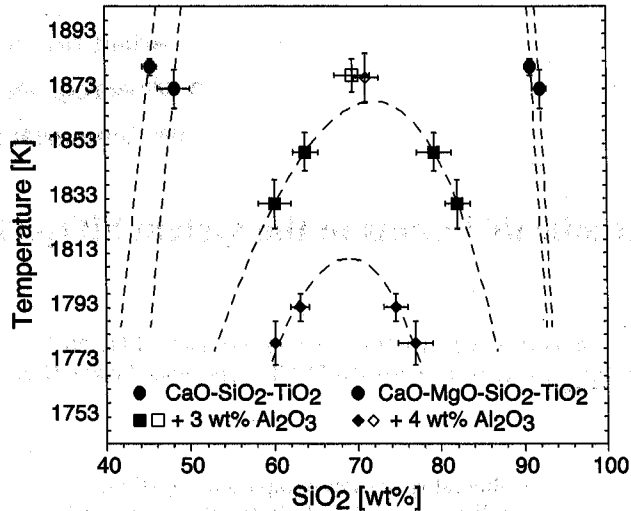


Fig. 1. SiO₂ content of quenched coexisting liquids in the CaO-MgO-SiO₂-TiO₂-Al₂O₃ system. Open symbols indicate quench of a homogeneous liquid. Addition of 3 wt% and 4 wt% Al₂O₃ reduces dramatically the consolute temperature and the extension of the miscibility gap of the Al-free melt (filled circles). In bulk compositions with 6 wt% Al₂O₃ no stable liquid-liquid boundary was found, and phase separation is rendered metastable.

the solution and k is a real number. Equation (1) includes and generalizes the Kohler (1960) extrapolation (*i.e.* $k = 1$ for subregular solution parameters). This approach overcomes the problem of fitting a ternary parameter in systems where experimental data are scarce and provides a flexible description of the extrapolated excess function at very low dilution. With equation (1), the excess free energy surface has been successfully modelled in the CaO-SiO₂-TiO₂ system. We conducted quench experiments of coexisting liquids in the CaO-MgO-SiO₂-TiO₂-Al₂O₃ system in order to expand the model to higher orders. Compositions of coexisting liquids are of special interest because they permit direct determination of the excess parameters of the liquid without interference of the solids or chemical potentials of the solution end-members. Our experiments confirm the dramatic decrease of consolute temperature and size of the miscibility gap in these liquids when few mol% Al₂O₃ is added (*e.g.* Wood & Hess, 1980). SiO₂ content of coexisting liquids from these experiments versus temperature is plotted in Fig. 1 for 0 wt%, 3 wt% and 4 wt% Al₂O₃ in the bulk composition. The emphasis of the present paper is to illustrate the formal difficulties that arise when the SiO₂-TiO₂ miscibility gap is extrapolated to Al-bearing silicate liquids with conventional

excess functions using an additional ternary parameter. To investigate the extrapolation of the SiO₂-TiO₂ miscibility gap in Al-bearing liquids, we use the ternary SiO₂-TiO₂-Al₂O₃ system as a model system.

In order to determine non-ideal contributions to the free energy of the melt, experimental liquidus data have to be evaluated in subsystems where no stable solvus exists and direct activity measurements are scarce. Points on the phase boundary are defined by identical chemical potentials of the components in coexisting phases $\mu_i(1) = \mu_i(2)$ where $\mu_i = \mu_i^0 + RT \ln(a_i)$ (μ_i^0 denotes the chemical potential at standard state and a_i the activity of end-member i in the solution). Neglecting deviations from stoichiometric compounds, the free energy of the crystalline solid is computed at ambient pressure from standard state enthalpy and entropy H^0 and S^0 and the specific heat capacity C_p : $\Delta_f G(T) = H^0 - TS^0 + \int_{C_p} dT - T \int (C_p/T) dT$. This expression has to be extrapolated to liquidus temperatures in order to constrain the free energy of the melt. In some cases, lack of experimental data on the specific heat capacity at high temperatures leads to a large range of possible $\Delta_f G(T)$ of the solids depending on which $C_p(T)$ polynomial is used, *i.e.* polynomials involving a linear T -term (Fei & Saxena, 1987) or not

(Berman & Brown, 1985). In these cases, the estimation of excess parameters of the melt based on liquidus data depends on thermochemical parameters of the solids and the $C_p(T)$ function used (e.g. databases from Robie *et al.*, 1978; Berman & Brown, 1985; Holland & Powell, 1990). On the other hand, compositions of coexisting liquids yield direct constraints to the excess function, because two (or more) liquids are in equilibrium. In this case, phase-equilibrium is described with $\mu_i(\text{melt } 1) = \mu_i(\text{melt } 2)$. This relation reduces to direct constraints of non-ideal excess parameters, because the standard state chemical potentials of the end-members cancel in the equation. Thus, the calculations of miscibility gaps represent an excellent test for solution models in silicate liquids at high temperatures.

In order to model the excess Gibbs free energy of the ternary $\text{SiO}_2\text{-TiO}_2\text{-Al}_2\text{O}_3$ system from binary subsystems, we fitted binary excess parameters to published liquidus data in the $\text{SiO}_2\text{-Al}_2\text{O}_3$, $\text{SiO}_2\text{-TiO}_2$ and $\text{TiO}_2\text{-Al}_2\text{O}_3$ systems. No data on coexisting liquids above the solidus temperature in the $\text{SiO}_2\text{-TiO}_2$ and $\text{SiO}_2\text{-TiO}_2\text{-Al}_2\text{O}_3$ systems have been found in the literature. To determine the extension of the miscibility gap and further refine the excess parameters of the melt with solvus data, we synthesized and quenched coexisting $\text{SiO}_2\text{-TiO}_2\text{-Al}_2\text{O}_3$ liquids from temperatures above the liquidus surface. Finally we will present fitted excess parameters of equation (1) which avoids addition of a ternary term when extrapolated to the ternary system. The modelled excess surface reproduce the

ternary miscibility gap in detail and yield a valuable approximation of the excess Gibbs free energy of the melt when extrapolated outside the region of liquid immiscibility.

Assessment of binary and ternary systems

Margules-type excess parameters ($G^{xs} = x_1x_2[W_{112}x_1 + W_{122}x_2]$, where $W = W_H - TW_S$ is temperature dependent) have been fitted to binary solvus and liquidus data in the system $\text{CaO-MgO-SiO}_2\text{-Al}_2\text{O}_3\text{-TiO}_2$ with linear programming methods. We prefer this optimization procedure, because most experimental liquidus data are quench experiments, resulting in half brackets for the actual equilibrium state and convert easily to inequality equations for fit parameters. To evaluate a set of inequalities, linear programming is clearly indicated (see Berman *et al.*, 1986, and Engi, 1993, for discussion). Standard state enthalpies and entropies for the crystalline phases are taken from Berman (1988), Berman & Aranovich (1996) and Barin (1993), $C_p(T)$ coefficients from Berman & Brown (1985), Berman (1988) and Eriksson & Pelton (1993a and b), because they use the same conservative $C_p(T)$ polynomial. For the liquid oxides we used C_p values from Richet *et al.* (1982, SiO_2), Courtial & Richet (1993, Al_2O_3) and Chase *et al.* (1985, TiO_2). We favoured these data over other published partial molar heat capacities of multicomponent liquids (e.g. Stebbins *et al.*, 1984, and Lange & Navrotsky, 1992), because the TiO_2 content of the liquids considered for C_p measure-

Table 1. Standard-state thermodynamic properties of solid and liquid oxides.

Mineral	abbrev.	formula	H^0 [J/mol]	S^0 [J/Kmol]	reference
"Tieilite"	AlT1	Al_2TiO_5	-2617080.42	109.6210	this study ¹
Corundum	Cor	Al_2O_3	-1675699.95	50.8200	Berman (1988)
α -Cristobalite	a-Crist	SiO_2	-907753.35	43.3943	Berman (1988)
β -Cristobalite	b-Crist	SiO_2	-906377.23	46.0288	Berman (1988)
Mullite (stoech.)	Mul	$\text{Al}_6\text{Si}_2\text{O}_{13}$	-6823487.97	274.9000	this study ²
α -Quartz	a-Qz	SiO_2	-910699.95	41.4600	Berman (1988)
β -Quartz	b-Qz	SiO_2	-908626.77	44.2068	Berman (1988)
Rutile	Rut	TiO_2	-944750.00	50.8800	Berman & Aranovich (1996)
low-Tridymite	l-Trid	SiO_2	-907749.56	43.7702	Berman (1988)
high-Tridymite	h-Trid	SiO_2	-907045.12	45.5237	Berman (1988)
SiO_2 liq		SiO_2	-915982.73	19.8613	this study
TiO_2 liq		TiO_2	-943848.47	16.5329	this study
Al_2O_3 liq		Al_2O_3	-1667690.00	0.2628	this study

¹ S^0 from Barin (1993), ² S^0 from Eriksson & Pelton (1993a),

$T^0 = 298 \text{ K}$, $p^0 = 10^5 \text{ Pa}$

Table 2. Cp coefficients used in this study.

Mineral	k1	k2	k3	k4	k8	reference
"Tieilite"	249.2900	0	-4806100.	-1350.100	516030000.	Berman & Brown (1985)
Corundum	155.0189	0	-3861363.	-828.387	409083648.	Berman & Brown (1985)
α -Cristobalite	83.5136	0	-2455360.	-374.693	280072192.	Berman & Brown (1985)
β -Cristobalite	83.5136	0	-2455360.	-374.693	280072192.	Berman & Brown (1985)
Mullite (stoech.)	634.8100	0	-17209900.	-3373.500	2122740000.	Berman & Brown (1985)
α -Quartz	80.0120	0	-3546684.	-240.276	491568384.	Berman & Brown (1985) ¹
β -Quartz	80.0120	0	-3546684.	-240.276	491568384.	Berman & Brown (1985)
Rutile	77.8376	0	-3367841.	0	402940672.	Berman & Brown (1985)
low-Tridymite	75.3727	0	-5958095.	0	958246144.	Berman (1988)
high-Tridymite	75.3727	0	-5958095.	0	958246144.	Berman (1988)
SiO ₂ liq	81.3730	0	0	0	0	Richet <i>et al.</i> (1982)
TiO ₂ liq	100.4160	0	0	0	0	Chase <i>et al.</i> (1985)
Al ₂ O ₃ liq	130.2000	0.0357	0	0	0	Courtial & Richet (1993)

note: Cp function used in this study: $C_p = k_1 + k_2T + k_3/T^2 + k_4/\sqrt{T} + k_8/T^3$ in J/Kmol
¹: λ transition modelled with additional $C_p = (-0.09186959 + 0.00024607 T)^2$ between [373K, 848K], Berman & Brown (1986).

ments and subsequent linear regression did not exceed 0.34 and was lower in most samples. However, the adopted Cp values of pure SiO₂ and TiO₂ are lower but within the error limits of the partial molar heat capacities of Lange & Navrotsky (1992). Courtial & Richet (1993) observed a temperature-dependent partial molar heat capacity of liquid Al₂O₃ in the system MgO-SiO₂-Al₂O₃ which is consistent with the Cp value at very high temperature given by Chase *et al.* (1985) for pure Al₂O₃. There is no explicit excess heat capacity in this study. Thermochemical values used are given in Tables 1 and 2. Excess entropy terms of the liquid were minimized and omitted whenever possible. No stable liquid miscibility gap has been observed for the systems SiO₂-Al₂O₃ and TiO₂-Al₂O₃. For these binaries, the non-ideal contributions to the free energy of the melt was estimated from published liquidus data. At this point we emphasize again that evaluation of liquidus data represent indirect constraints on the free energy of the liquid. The calculated solution parameters in systems without stable liquid-liquid immiscibility are therefore considered as first-order approximations.

SiO₂-Al₂O₃

After the first studies in this system by Bowen & Greig (1924), numerous authors (Aramaki & Roy, 1959; Welch, 1960; Davis & Pask, 1972; Aksay & Pask, 1975) published additional experimental liquidus data. Melting points of pure SiO₂

and Al₂O₃ at 1999 ± 5 K and 2327 ± 8 K were adopted (Chase *et al.*, 1985). The eutectic point at $x(\text{Al}_2\text{O}_3) = 0.045 \pm 0.20$, 1868 K has been confirmed (Aramaki & Roy, 1959), but contradictory results about stoichiometry and melting of mullite have been reported. In the following we will denote mullite with 2SiO₂.3Al₂O₃ and SiO₂.2Al₂O₃ stoichiometry as 2:3-mullite and 1:2-mullite, respectively. Aramaki & Roy (1959) determined congruent melting of 2:3-mullite at 2123 ± 15 K, but Welch (1960) reported incongruent melting of 1:2-mullite at 2153 K. Klug *et al.* (1987) reviewed the data and conducted additional experiments on the mullite melting. They favoured peritectic 1:2-mullite melting at 2163 K and documented the shift in stoichiometry from 2:3 at low temperatures to almost 1:2 at liquidus temperatures. Their results agree with the phase diagram of Welch (1960) and even with the detailed run reports of Aramaki & Roy (1959), because Aramaki & Roy (1959) did not rule out a possible shift of the mullite composition to higher Al₂O₃ content at liquidus temperatures. Discrepancy in alumina liquidus determinations has been explained by the influence of starting materials and experimental methods employed (Schneider, 1994). Studies from Horibe & Kuwubara (1967) and ternary Cr₂O₃-Al₂O₃-SiO₂ data from Roeder *et al.* (1968) confirm the alumina-mullite-liquid invariant point from Welch (1960) and Aramaki & Roy (1959) at $x(\text{Al}_2\text{O}_3) = 0.64$ and 0.66, respectively. We used the data from Aramaki & Roy (1959) for stoichiometric 2:3-mullite melting and the alumina liq-

Table 3. Margules excess parameters used in this study.

	W_H	W_S	k
SiO ₂ -TiO ₂			
112	26054.226	-5.456	-3
122	70487.320	9.453	-3
Al ₂ O ₃ -TiO ₂			
112	-1330.153	0	1
122	-2108.769	0	1
Al ₂ O ₃ -SiO ₂			
112	620798.585	288.902	1
122	179127.605	90.331	1

note: the ternary excess Gibbs free energy is
 $G^{xs} = \sum (x_1 + x_2)^{-k} [x_1 x_2 (W_{112} x_1 + W_{122} x_2)]$
 where $W = W_H - TW_S$ in J/mol, T in K.

uidus from Horibe & Kuwubara (1967) which is consistent with the work of Aramaki & Roy (1959). Their phase-equilibrium data are considered thermodynamically stable (Schneider, 1994), because they used α -Al₂O₃ as part of the starting material. Fitted Margules excess parameters are listed in Table 3 and the calculated phase diagram is shown in Fig. 2a. Neglecting of the compositional shift to 2:1 mullite leads to a calculated melting at 2141 K.

Metastable immiscibility in SiO₂-Al₂O₃

Several studies indicate at least one subliquidus miscibility gap from thermodynamic analysis of the liquidus line (Risbud & Pask, 1977; Hillert & Jonsson, 1992; Djuric *et al.*, 1996; Ban *et al.*, 1996). MacDowell & Beall (1969), Galakhov *et al.* (1976) and Jantzen & Herman (1979) observed unmixing of annealed glasses. Recently, Sayir & Farmer (1995) observed *in situ* liquid-liquid immiscibility during crystal growth of mullite. The dashed line in Fig. 2a indicates the calculated binodal at subliquidus temperatures from this study ($T_c = 2027$ K near $x(\text{Al}_2\text{O}_3) = 0.748$). The low Al branch is in agreement with studies of MacDowell & Beall (1969) but disagrees with separation data from Galakhov *et al.* (1976). Consolute temperature and extension of the calculated immiscibility region depend strongly on the temperature dependency of the excess parameter (linear in this study: $W = W_H - TW_S$, Ban *et al.* (1996) used Redlich-Kister polynomial coefficients with a reciprocal T-dependence). The fitted $W_{S122} = 289$ J/molK for the liquidus temperature range is considered a first-

order approximation and the calculated subliquidus miscibility gap of the melt as a rough approximation of observed phase separation tendency in glasses. However, there is evidence for the extension of the metastable miscibility gap to high Al₂O₃ (McPherson, 1980: $T_c = 1473 - 1673$ K; Beriman & Brown, 1984: $T_c = 2096$ K; Hillert & Jonsson, 1992: T_c near 1900 K and Eriksson & Pelton, 1993a: $T_c = 1586$ K). Recent studies suggest that micro-phase separation of the liquid precedes the formation of mullite in aluminosilicate melts (Sayir & Farmer, 1995; Okada *et al.*, 1995).

TiO₂-Al₂O₃

Fusion experiments in this system have been reported by Lang *et al.* (1952). They confirmed two eutectic points at 0.16 Al₂O₃, 1978 K and 0.56 Al₂O₃, 2123 K and congruent melting of Al₂TiO₅ ("teillite", *e.g.* Langton, 1976) at 2133 K from earlier studies (Wartenberg & Reusch, 1932; Bunting, 1933). Their results are in agreement with phase relations in the ternary system BeO-TiO₂-Al₂O₃ (Lang *et al.*, 1952) and ZrO₂-TiO₂-Al₂O₃ (Levin *et al.*, 1964, p. 262). No additional interoxide compound has been reported. Melting of pure TiO₂ was assumed at 2133 ± 20 K (Chase *et al.*, 1985). Refined temperature-independent excess parameters are given in Table 3. The calculated phase diagram is plotted in Fig. 2b together with experimental data.

SiO₂-TiO₂

For the system SiO₂-TiO₂ experimental data showing the existence of a miscibility gap are available from DeVries *et al.* (1954), McTaggart & Andrews (1957), Massazza & Sirchia (1958) and Galakhov *et al.* (1974). DeVries *et al.* (1954) located the eutectic between $x(\text{TiO}_2) = 0.077$ and 0.083 at 1823 K. At 2053 K two liquids are stable within the compositional limits $x(\text{TiO}_2) = 0.158 \pm 0.02$ and $x(\text{TiO}_2) = 0.896 \pm 0.02$. Massazza & Sirchia (1958) investigated the liquidus at 1873 K refining the position of the eutectic point between $x(\text{TiO}_2) = 0.069$ and 0.093. McTaggart & Andrews (1957) studied the binary system in the course of an investigation of the ZrO₂-SiO₂-TiO₂ system. Their results are in substantial agreement with those reported by DeVries *et al.* (1954): the limits of the two-liquid field were placed at $x(\text{TiO}_2) = 0.150$ to 0.167 and $x(\text{TiO}_2) = 0.909$ to 0.935 at 2038 K. Circone & Agee (1995) determined compositions of coexisting liquids at 3.0 GPa and tem-

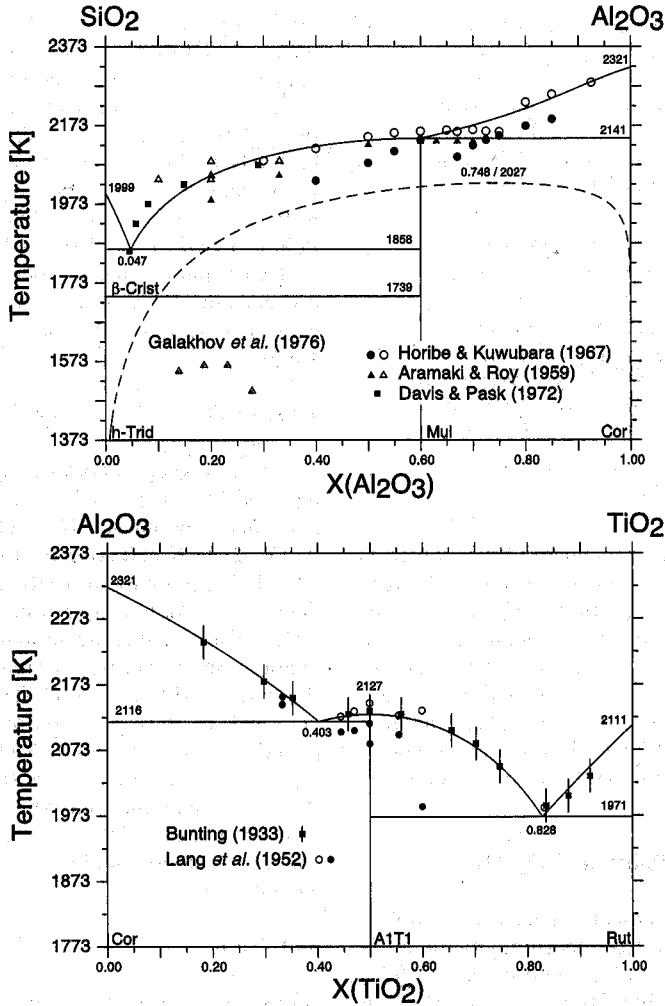


Fig. 2. Calculated phase diagrams for the $\text{Al}_2\text{O}_3\text{-SiO}_2$ (a) and $\text{Al}_2\text{O}_3\text{-TiO}_2$ (b) systems. Critical quench experiments are considered from Aramaki & Roy (1959), fusion experiments from Bunting (1933), Lang *et al.* (1952), Horibe & Kuwubara (1967), and mullite liquidus data from diffusion experiments (Davis & Pask, 1972). Slashed triangles denote unmixing experiments in glasses from Galakhov *et al.* (1976). Open symbols indicate one liquid and filled symbols liquid + crystalline phase stable. The dashed line indicate the calculated binodal of the solvus at subliquidus temperatures. Numbers denote calculated temperatures of phase transitions. Klüg *et al.* (1987) documented the compositional shift of mullite from $2\text{SiO}_2\cdot 3\text{Al}_2\text{O}_3$ to $1\text{SiO}_2\cdot 2\text{Al}_2\text{O}_3$ at liquidus temperature, which is not modelled with the stoichiometric approach in this calculation.

peratures from 2373 to 2593 K. Their results show a dramatic asymmetric shift of the liquid miscibility gap to the SiO_2 -rich side. No data on coexisting $\text{SiO}_2\text{-TiO}_2$ liquids above 2100 K at ambient pressure have been reported so far. The calculated phase diagram is shown in Fig. 3 together with liquidus data from the literature and solvus data from this study.

$\text{Al}_2\text{O}_3\text{-SiO}_2\text{-TiO}_3$

Quench experiments in the ternary $\text{Al}_2\text{O}_3\text{-SiO}_2\text{-TiO}_2$ system have been reported by Agamawi & White (1952) for the high-silica corner and along the $\text{SiO}_2\text{-Al}_2\text{TiO}_5$ join, indicating a peritectic at $(x_{\text{SiO}_2}, x_{\text{Al}_2\text{O}_3}, x_{\text{TiO}_2}) = (0.8487, 0.0516, 0.0997)$, 1753 K and an eutectic invariant point at

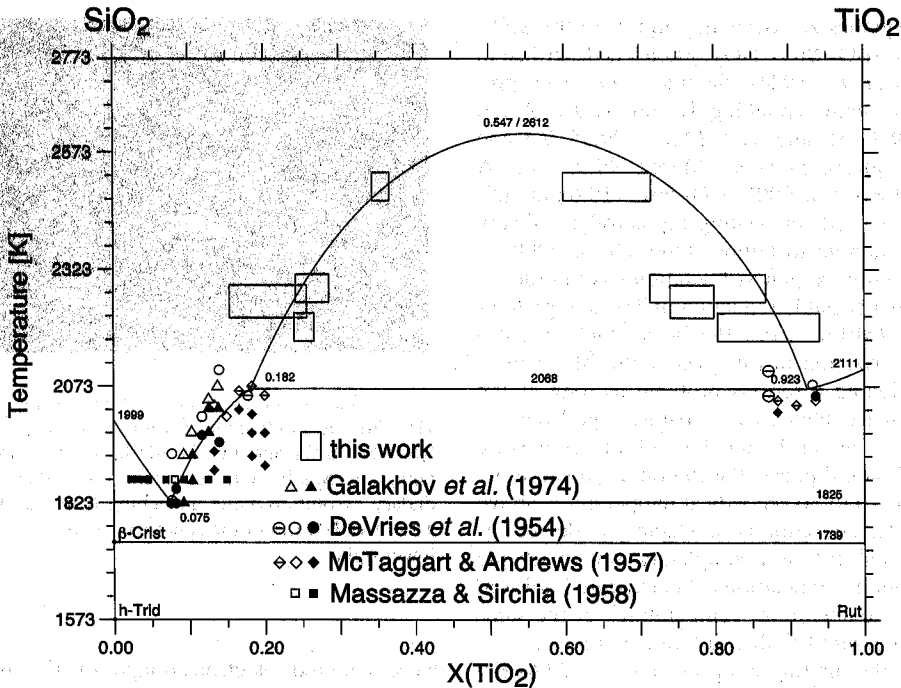


Fig. 3. Calculated phase diagram for the $\text{SiO}_2\text{-TiO}_2$ system. Symbols refer to critical quench experiments from DeVries *et al.* (1954), McTaggart & Andrews (1957) and Massazza & Sirchia (1958) that have been used to constrain non-ideal solution parameters with liquidus and solvus data. Triangles point liquidus experiments from Galakhov *et al.* (1974). Filled symbols indicate quenched crystalline + liquid phases stable, open symbols denote one liquid, slashed symbols two liquids. Additional solvus data of this work are plotted within 1σ boxes in composition and temperature. Numbers denote calculated temperatures of phase transitions.

(0.8443, 0.0472, 0.1085), 1743 K. No ternary oxide compound has been detected and no data on the miscibility gap above liquidus temperature was found in the literature. Due to lack of data on the miscibility gap at low Al concentration, we decided to determine the compositions of coexisting liquids in this ternary system.

Experimental methods and results

In the course of a systematic study of the liquid miscibility gap in the $\text{CaO-MgO-SiO}_2\text{-TiO}_2\text{-Al}_2\text{O}_3$ system, we determined compositions of coexisting liquids quenched from 1750 to 1920 K with a Rh/Pt resistance furnace at Basel. Experimental details are reported elsewhere (Kirschen, 1998). In order to determine the extension of the $\text{CaO-MgO-SiO}_2\text{-TiO}_2$ liquid miscibility gap in Al-bearing systems, we added 3 to 9 wt% Al_2O_3 to bulk compositions inside the stable two-liquid

field. The dramatic decrease of the liquid miscibility gap at very low Al_2O_3 content is shown in Fig. 1. Liquid immiscibility in the ternary $\text{SiO}_2\text{-TiO}_2\text{-Al}_2\text{O}_3$ system could not be investigated at Basel, because our quench experiments with the Rh/Pt resistance furnace are restricted to temperatures below 2000 K in air.

Recently, a laser heating technique has been developed at the Centre de Recherches sur les Matériaux à Haute Température CRMHT Orléans that permits NMR, EXAFS and solidification process studies on oxide samples at temperatures above 2000 K with variable oxygen potential (Coutures *et al.*, 1994). The container-free heating process grants the absence of contamination of the sample with container material and heterogeneous crystallization of homogeneous samples when quenched. It is an appropriate technique to quench coexisting TiO_2 -rich and TiO_2 -poor liquids from very high temperatures with sufficiently high cooling rates (> 300 K/s). The levitation set-up

used to synthesize coexisting liquids in the $\text{SiO}_2\text{-TiO}_2$ and $\text{Al}_2\text{O}_3\text{-SiO}_2\text{-TiO}_2$ systems is described in Coutures *et al.* (1994). Samples have been prepared from commercial highly pure oxides (Al_2O_3 Fluka 99.99 % and TiO_2 Merck 99.95 %) and crushed quartz powder (Merck 99.95 %). A Coherent Everlase 600W CO_2 laser (10.6 μm radiation) was used for heating the aerodynamically levitated sample to temperatures above 2000 K. We used pure oxygen as levitation gas in order to minimize a possible reduction of Ti^{4+} at high temperatures (Millot *et al.*, 1987). For SiO_2 -rich liquids, vaporization of SiO_2 was noticeable. This is not considered a serious problem as long as the run product contains two separate liquid phases. In order to avoid a total loss of the coexisting SiO_2 -rich liquid phase, the run duration had to be limited to 10 to 30 seconds at temperatures above 2200 K. This duration is satisfactory to detect liquid immiscibility in a completely molten sample and to obtain compositions of coexisting liquids at very high temperature. Temperatures of the sample are measured with a 0.4 μm pyrometer calibrated at the melting point of alumina (2326 K). No correction to the Al_2O_3 emissivity has been applied. During the heating interval the powder sample was completely molten and stabilized in the levitation jet. A sharp decrease of the pyrometer signal indicates the shut off of the laser followed by a typical radiative cooling of the sample. After the laser shut off, pyrometer signals simultaneously measured at 4 different wavelengths indicate a homogeneous temperature of the sample. This temperature has been interpreted as the actual temperature of the sample during the run. A detailed description of the temperature measurement and an estimate of the temperature errors is given in Coutures *et al.* (1994). The quenched products were optically checked, cut and polished for electron-microprobe (EMP) analysis. Compositions of glassy phases were determined by EMP analysis with a JEOL JXA 8600 Superprobe at Basel University. Data collection conditions were 15 kV, 10 nA and measuring times from 10 to 20 s. To estimate the homogeneity of the quenched glasses, about 50 measurements per phase have been collected with a 5 to 15 μm defocused electron beam. Natural rutile (100 wt% TiO_2) and orthoclase (64.57 wt% SiO_2 , 17.35 wt% Al_2O_3) served as standards for Ti, Si and Al. Proza correction (Bastin & Heijligers, 1990) has been applied for raw data reduction. Microprobe measurements with totals between 98 to 102 wt% have been averaged. Measured impurities of Ca, Mg, Fe, Na, K are less than 0.2 wt% in total. A

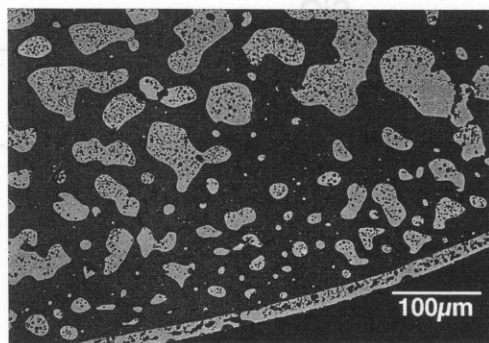


Fig. 4. Back-scattered electron image of quench ST1-1H. The TiO_2 -rich liquid (bright) is clearly separated from the SiO_2 -rich matrix (dark) by a sharp phase boundary. Small SiO_2 -rich inclusions indicate a secondary exsolution while quenching from 2500 K. The TiO_2 enriched rim of the spherical sample is seen at the lower right.

back-scattered electron image of the polished sphere of run ST1-1H is shown in Fig. 4. Two liquids are clearly separated by a sharp phase boundary. The TiO_2 -rich glass shows inclusions of a SiO_2 -rich phase indicating secondary exsolution while quenching from high temperature. Considering the size of a TiO_2 -rich liquid inclusion as characteristic length scale $l = 100 \mu\text{m}$ and $t = 1 \text{ s}$ as typical time scale for the quench, the diffusion coefficient is estimated to $D = l^2/t = 10^{-4} \text{ cm}^2/\text{s}$. Compared to reported coefficients of diffusion in silicate liquids ($D < 10^{-4} \text{ cm}^2/\text{s}$, see Chakraborty, 1995) the formation of two coexisting liquid phases as unmixing of a homogeneous sample during the quench is excluded on a length scale of 100 μm . However, the observed formation of secondary exsolution of the TiO_2 -rich liquid within a length scale of $l = 1 \mu\text{m}$ is consistent with diffusion rates of the order of magnitude $D = 10^{-8} \text{ cm}^2/\text{s}$ for network-forming cations in silicate melts. The EMP electron beam was slightly defocused in order to determine the average composition of the TiO_2 -rich glass. Within standard deviation of the measurements no compositional gradient from centre to rim was observed for the SiO_2 -rich liquid nor for the TiO_2 -rich liquid for which the scattering of the EMP measurements is significantly higher due to secondary exsolution. We exclude therefore a considerable temperature gradient from centre to rim during the synthesis of the samples. Standard deviations range from 1.2 to 6.2 wt% for $\text{SiO}_2\text{-TiO}_2$, from 0.8 to 3.0 wt% for

Table 4. Compositions of quenched liquids in the system $\text{SiO}_2\text{-TiO}_2\text{-Al}_2\text{O}_3$.

run id.	T [K]	wt% SiO_2 (1 σ)	wt% TiO_2 (1 σ)	wt% Al_2O_3 (1 σ)	total	n
ST 1-1H	2500 \pm 30	57.49(1.20)	42.16(1.20)		99.66	49
		28.70(5.34)	72.10(5.23)		100.80	47
ST 1-2H	2280 \pm 30	67.91(2.58)	32.37(2.28)		100.28	50
		5.55(1.79)	94.51(1.72)		100.24	28
ST 2-1H	2250 \pm 30	74.61(5.97)	25.49(6.21)		100.10	67
		18.47(2.45)	82.23(3.04)		100.84	30
ST 3-1H	2200 \pm 30	68.81(1.46)	31.40(1.49)		100.21	43
		10.10(5.50)	90.62(5.58)		100.76	47
STA1-1H	2080 \pm 30	55.66(1.57)	40.36(1.67)	4.22(0.95)	100.25	63
		10.90(1.51)	85.68(1.63)	4.41(0.87)	100.99	28
STA1-2H	2070 \pm 30	55.34(0.83)	40.96(1.04)	4.26(0.64)	100.56	14
		11.53(3.00)	84.78(3.04)	4.44(1.05)	100.80	29
STA2-2H ¹	2050 \pm 30	13.64(0.53)	72.70(0.66)	13.77(0.39)	100.11	36
STA3-1H ¹	2070 \pm 30	33.12(0.35)	53.71(1.05)	13.43(0.15)	100.27	33
STA3-2H ¹	2050 \pm 30	33.05(0.31)	53.70(0.59)	13.17(0.16)	99.93	40
STA4-2H ¹	1970 \pm 30	51.53(0.73)	34.65(0.54)	13.82(0.17)	100.01	58
STA5-2H ¹	2230 \pm 30	59.24(0.58)	19.81(0.44)	21.83(0.33)	100.88	10

¹: one liquid.

Al-bearing unmixed glasses and are significantly lower for homogeneous glasses. Measured compositions of coexisting liquids in $\text{SiO}_2\text{-TiO}_2$ and $\text{SiO}_2\text{-TiO}_2\text{-Al}_2\text{O}_3$ systems are listed with 1 σ standard deviations in Table 4 and plotted in Fig. 3 and Fig. 6, respectively.

Model results

The experimentally determined liquid miscibility gap of the $\text{SiO}_2\text{-TiO}_2$ system is in general agreement with previously published quench data at liquidus temperatures from DeVries *et al.* (1954) and McTaggart & Andrews (1957) (see Fig. 3). The miscibility gap is almost symmetrical within experimental uncertainty. A two-parameter Margules excess polynomial fits the solvus results with temperature-independent $W_{112} = 40.3 \pm 3.4$ kJ and $W_{122} = 44.8 \pm 4.7$ kJ (1 = SiO_2 , 2 = TiO_2). These values are independent of the chemical potentials of the solution end-members of the melt when derived from solvus data, because μ_i^0 cancel in the equations when two phases of the same solution coexist. However, modelling of additional liquidus data requires a slightly asymmetric and temperature-dependent excess function for the melt ($W = W_H - TW_S$, see Table 3). Calculated enthalpy of fusion (112.6 kJ) of Al_2O_3 are in agreement with published values (e.g. Richet &

Bottinga, 1986: 107.5 ± 5.4 kJ). Liquid SiO_2 parameters fitted to solvus and liquidus data in the $\text{SiO}_2\text{-TiO}_2$ system yield $\Delta_{\text{fus}}H = 12.8$ kJ, higher than reported (e.g. Richet *et al.*, 1982: 8.9 ± 1.0 kJ; Berman & Brown, 1984: 12.5 kJ). Using a 5-parameter $\text{SiO}_2\text{-TiO}_2$ excess polynomial and constraining $\Delta_{\text{fus}}H$ to 8.9 ± 1.0 kJ we could not resolve the linear problem. We doubt that this discrepancy is solely due to shortcomings of the applied excess function because (1) fitted excess terms are in agreement with measured solvus data, and (2) the temperature range of liquidus constraints used in this study considerably exceeds the calibration range of Berman's (1988) mineral data for cristobalite and rutile. However, the calculation of the ternary miscibility gap is not sensitive to the chemical potentials of the solution end-members, but depends on the polynomial degree of the binary excess function used. The $\text{SiO}_2\text{-TiO}_2$ excess terms dominate the calculated ternary miscibility gap, because the influence of the Al_2O_3 excess terms is of minor importance at very low Al_2O_3 content. To reproduce our experimental data, we weight the binary excess terms with $(x_1 + x_2)^k$ (equation 1).

Extrapolation of the $\text{SiO}_2\text{-TiO}_2$ parameters with positive k values resulted in calculated miscibility gaps that are in clear disagreement with our experiments (see calculated miscibility gaps in Fig. 6). k values for the Al_2O_3 binaries have

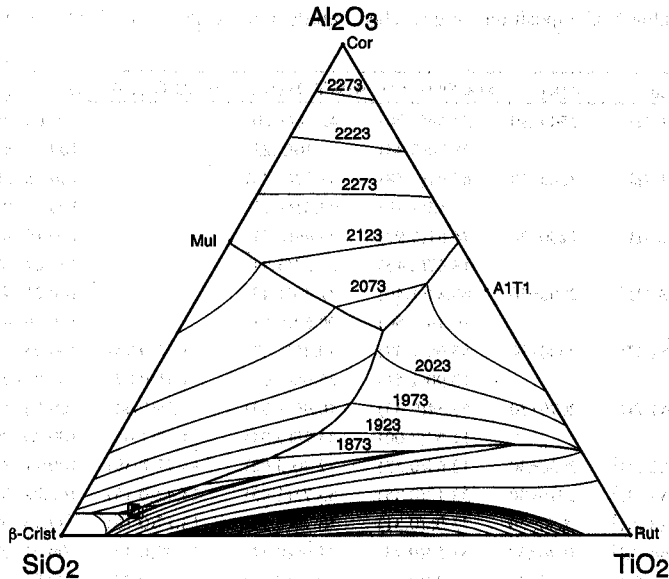


Fig. 5. Calculated phase diagram for the SiO_2 - TiO_2 - Al_2O_3 system. Isotherms are shown from $T = 1773$ K, to 2623 K, with 50 K increments. Squares point reported ternary invariant compositions from Agamawi & White (1952) (their figure 10: E, 1743 K; R, 1753 K). Liquid-liquid unmixing is stable at temperatures above 2053 K.

been estimated with liquidus data from Agamawi & White (1952). The Al_2O_3 - SiO_2 and Al_2O_3 - TiO_2 excess parameters have only a minor influence on the decline of the SiO_2 - TiO_2 miscibility gap at low $x_{\text{Al}_2\text{O}_3}$. A consistent modelling of all our experiments on the ternary miscibility gap and reported liquidus data could be obtained with $k = -3$ for SiO_2 - TiO_2 , $k = 1$ for Al_2O_3 - TiO_2 and Al_2O_3 - SiO_2 binaries. No ternary parameter had to be included. $k = -3$ for the SiO_2 - TiO_2 binary indicates that an excess polynomial of degree 6 or greater is required for extrapolation purposes. The calculated ternary phase diagram is plotted in Fig. 5 together with reported invariant points from Agamawi & White (1952). The coincidence between calculation and experimental invariant points is excellent: differences are estimated to be smaller than 15 K and 3 mol%. Main discrepancies remain for the mullite melting, possibly due to our 2:3 stoichiometric approach.

Discussion

The sharp decline of the stable liquid miscibility gap at low Al_2O_3 content is an excellent example to illustrate the difficulties that arise when

fitting an additional ternary excess parameter in order to adjust the extrapolated binary excess functions. In Fig. 6 calculated ternary miscibility gaps at 2073 K are shown (1) without correction to the binary excess parameters $G^{xs} = \sum x_i x_j (W_{ij} x_i + W_{ij} x_j)$ where $i, j = 1, 2, 3$ (dashed line, $k = 0$ in equation (1) for all binary systems), (2) extrapolated with the Kohler (1960) method (dotted line, $k = 1$ in equation (1) for all binary systems) and (3) with addition of a ternary parameter $W_{123} = -200$ kJ/mole to binary excess parameters (dash-dotted line). The calculated miscibility gap at 2073 K with $k = -3$ for the SiO_2 - TiO_2 excess function is plotted in Fig. 6 as solid line for comparison. With the Kohler model (case 2), the extent of the calculated miscibility gap decreases due to increasing interference with negative Al_2O_3 - SiO_2 and Al_2O_3 - TiO_2 excess free energy terms. In the third case, the excess Gibbs free energy is $G^{xs} = \sum x_i x_j (W_{ij} x_i + W_{ij} x_j) + W_{123} x_1 x_2 x_3$, where the ternary parameter W_{123} is calculated from the binary excess parameters with a possible correction C_{123} : $W_{123} = 1/2 \sum (W_{ij} + W_{ji}) + C_{123}$ (Wohl, 1946 and Jackson, 1989). With a highly negative ternary parameter (e.g. $W_{123} = -200$ kJ/mole) the extrapolated positive SiO_2 - TiO_2 excess function is adapted towards consistency with the experimental data at low Al_2O_3 compositions. However, the asymmetry of

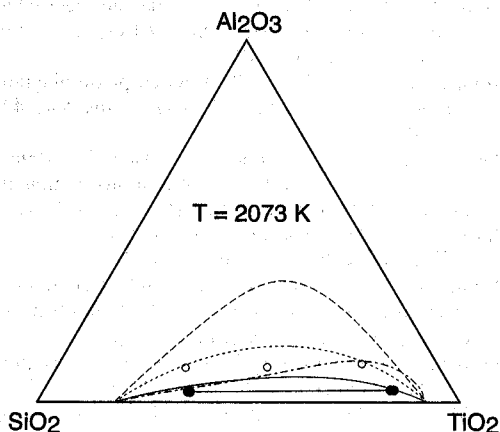


Fig. 6. Comparison of calculated miscibility gaps with experiments at 2073 K, 1 bar for the $\text{SiO}_2\text{-TiO}_2\text{-Al}_2\text{O}_3$ system for different methods of extrapolation. Regions of liquid immiscibility are calculated (1) without correction to the binary excess parameters $G^{xs} = \sum x_i x_j (W_{ij} x_i + W_{ij} x_j)$ where $i, j = 1, 2, 3$ ($k = 0$, dashed line), (2) extrapolated with the Kohler (1960) method ($k = 1$, dotted line), (3) with addition of a ternary parameter $W_{123} = -200$ kJ/mol to binary excess parameters (dash-dotted line) and with a generalized excess function (equation 1, $k = -3$, solid line). Solid spheres point to compositions of quenched coexisting liquids, open symbols denote quench of a homogeneous liquid. Mineral stability fields are omitted for clarity. Correction of binary $\text{SiO}_2\text{-TiO}_2$ excess terms with an additional ternary parameter results in an asymmetric decrease of the ternary miscibility gap, in disagreement with experiments.

the calculated miscibility gap increases with $|W_{123}|$ due to interference with highly contrary excess functions of the $\text{Al}_2\text{O}_3\text{-SiO}_2$ and $\text{Al}_2\text{O}_3\text{-TiO}_2$ binary systems (see Table 3). With experimental solvus and liquidus data in the ternary system, a feasible solution for the excess parameters could not be attained for the Wohl model. With addition of a ternary excess parameter to binary excess parameters alone, it was not possible to reproduce the experimental data, regardless of the value W_{123} .

Due to the increasing vaporization of SiO_2 in the containerless set-up at very high temperatures, the closure of the $\text{SiO}_2\text{-TiO}_2$ immiscibility dome could not be verified in this study. However, increasing TiO_2 solubility in the SiO_2 -rich liquid with temperature suggests the existence of an upper consolute point. Therefore, the application of a one-site subregular solution model to the $\text{SiO}_2\text{-TiO}_2$ binary is considered a formal assump-

tion, that permits a consistent modelling of all published phase-equilibrium data at ambient pressure in this system. An alternative description of liquid immiscibility may be based on two distinct melt structures (based on $\text{Si}^{[4]}$ - and $\text{Ti}^{[6]}$ - networks, respectively) with increasing solubility of the coexisting liquid phase at high temperature. Further experimental studies of Ti-bearing melts with *in situ* spectroscopic methods at high temperature may enlighten this question.

Using a two-parameter Margules excess function for the melt in the systems CaO-SiO_2 and MgO-SiO_2 , asymmetric solvus data and the characteristic minima of the free energy of mixing at orthosilicate composition is fairly well approximated (Kirschen, 1998). The interpretation of the fitted $\text{SiO}_2\text{-Al}_2\text{O}_3$ Margules excess polynomial as a subregular mixing model is difficult due to the composition and temperature dependent coexistence of $\text{Al}^{[4]}$, $\text{Al}^{[5]}$ and $\text{Al}^{[6]}$ in aluminosilicate liquids as observed by Poe *et al.* (1992). Because of this and that we are not yet able to give a theoretical basis of the *a priori* empirical Kohler weight factors ($x_1 + x_2$)- k , we do not interpret the fitted excess parameters in structural terms. As the constant heat capacities of pure SiO_2 and TiO_2 are extrapolated over a large temperature range, and because of the limited experimental liquidus data for the ternary system, we cannot convincingly exclude a small additional ternary interaction parameter of the melt from the assessment of liquidus data. However, we found a first-order approximation of the highly complex ternary excess function solely from binary excess terms with a minimum of excess parameters. The addition of a ternary parameter in order to adjust the extrapolated $\text{SiO}_2\text{-TiO}_2$ excess terms is not appropriate.

Conclusion

Coexisting liquids in $\text{SiO}_2\text{-TiO}_2$ and $\text{Al}_2\text{O}_3\text{-SiO}_2\text{-TiO}_2$ systems have been synthesized with a laser heated air-levitation set-up. EMP determined compositions of quenched liquids confirm the strong decline of the $\text{SiO}_2\text{-TiO}_2$ miscibility gap at 4 mol% Al_2O_3 content. At 10 mol% Al_2O_3 no liquid immiscibility has been detected above 1970 K. The results are in agreement with observations from *e.g.* Langton (1976) and Wood & Hess (1980).

The strong decline of the binary $\text{SiO}_2\text{-TiO}_2$ liquid miscibility gap in the $\text{Al}_2\text{O}_3\text{-SiO}_2\text{-TiO}_2$ system is used to exemplify problems that arise from existing extrapolation methods of binary excess

polynomials. Addition of ternary excess parameters in order to adjust the extrapolation of binary parameters to ternary data fails when the mole fraction of one component approaches low values. In this composition region the appropriate extrapolation of binary excess parameters is crucial. With separated weighting of binary Margules-type excess parameters, the measured immiscibility region in the ternary is reproduced in detail. Furthermore, extrapolation outside the stable miscibility gap to higher Al_2O_3 yields a valuable first-order approximation of the excess Gibbs free energy of the melt.

The application of the generalized excess function (1) on the $\text{CaO-SiO}_2\text{-TiO}_2$ system lead to k values for the binary excess parameters similar to this study: $k = 0, 1, -4$ for CaO-SiO_2 , CaO-TiO_2 , and $\text{SiO}_2\text{-TiO}_2$, respectively (DeCapitani & Kirschen, 1999). The liquid miscibility gap in the quaternary $\text{CaO-MgO-SiO}_2\text{-TiO}_2$ system could be reproduced in detail using similar k -values for the binary subsystems (Kirschen, 1998). Berman & Brown (1984) used $G^{\text{xs}} = x_1x_2(W_{112}x_1^2 + W_{1122}x_1x_2 + W_{1222}x_2^2)$ for the CaO-SiO_2 binary system in order to model the excess free energy in the $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3$ system. Because the calculated SiO_2 activity is almost identical to our first attempt using $G^{\text{xs}} = x_1x_2[W_{112}x_1 + W_{122}x_2]$, the Berman & Brown model is considered to be equivalent to a weighted extrapolation of binary solution terms $W_{112}x_1^2x_2$ and $W_{122}x_1x_2^2$ with $(x_1 + x_2)$, i.e. $k = -1$. These results suggest that k values of binary excess terms depend on the composition of the Al-bearing multicomponent system. In order to explore whether the k -values follow a systematic pattern, it is planned to expand calculation and experimental determination of coexisting liquids to the $\text{MgO-CaO-SiO}_2\text{-TiO}_2\text{-Al}_2\text{O}_3$ model system.

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