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Critical thermodynamic evaluation of oxide systems relevant to fuel ashes and slags: Potassium oxide–magnesium oxide–silica

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ABSTRACT

The K₂O–MgO–SiO₂ system has been thermodynamically assessed. The modified associate species model was applied to the liquid phase while the solubility of SiO₂ in K₂MgSiO₄ has been treated with a multi-sublattice model. The resulting new databank was used for the representation of the phase equilibria in the ternary system including several quasi-binary sections of the ternary diagram. The calculated phase relations are in good agreement with the experimental data. The phase equilibria in the unmeasured region were proposed on the basis of the obtained new databank.

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1. Introduction

In continuation of our previous works [1,2] the present work is dedicated to the critical thermodynamic evaluation of the ternary systems containing potassium, sodium, magnesium and silicon oxides. These constituents are found in many important technical materials, e.g. fuel ashes, slags, refractory products, glasses, fertilizers, etc. This system is also interesting for geological applications, because potash, magnesia and silica are among the most abundant constituents of igneous rocks and they are constituents of a variety of different magnesium minerals (forsterite, clinopyroxene, cordierite, etc). Although there is no naturally occurring mineral known consisting of K₂O, MgO and SiO₂ only, the phase equilibria and ternary compounds are important to petrology and mineralogy. The system is of importance for the chemistry of silicates formation and their stability. Knowledge of the limiting system K₂O–MgO–SiO₂ is essential to an understanding of the ternary system with water instead of potassium oxide, and of the quaternary system with alumina or with iron oxide.

The ternary system K₂O–MgO–SiO₂ was studied experimentally in the silica rich composition range [3,4]. A thermodynamic modelling approach can be useful for the description of the thermodynamic properties of the complex system, especially in case of such parts of the system, where experiments are complicated because of volatility and hygroscopicity of the alkali and high viscosity of the silicate

melts. CALPHAD type modelling now permits to treat the phase equilibria and the thermodynamic properties of such complex systems in their entirety.

The binary system K₂O–SiO₂ has previously been thermodynamically evaluated [1,5] and the new database has successfully been applied for the representation of phase relations and activity data. The liquid phase was described using the modified associate species model [6,7] which was considered as one of the most appropriate for complex liquids such as slags. It allows an adequate representation of the thermodynamic properties as well as the phase equilibria and can comparatively easily be adapted to meet the requirements of the respective systems. Furthermore, it provides an excellent basis for the modelling of slag viscosity [8].

The aim of the present work was the generation of a databank extended to the ternary system K₂O–MgO–SiO₂ along with the binaries systems K₂O–MgO and MgO–SiO₂. The ternary liquid is described using the above mentioned associate species model. For the solubility of SiO₂ in K₂MgSiO₄ the sublattice approach is chosen. The Gibbs energy parameters of the solid solution, ternary liquid and a number of stoichiometric compounds have been determined by optimisation on the basis of ternary experimental phase diagram and activity data, as far as they are available.

2. Experimental data

The phase diagram of the binary system MgO–SiO₂ was first studied by Bowen and Andersen [9] by analysis of quenched

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samples. The measurements revealed the existence of two stoichiometric compounds, forsterite (Mg_2SiO_4) which melts congruently at 1890 °C and protoenstatite (MgSiO_3) with incongruent (peritectic) melting at 1557 °C. The authors reported a miscibility gap in the SiO_2 -rich range of the liquid with a monotectic temperature of 1695 °C. Later investigations by Greig [10], Olshansky [11], and recently by Hageman and Oonk [12] confirmed the occurrence of immiscibility in the liquid, and the liquid–liquid boundaries were determined.

Schlaudt and Roy [13] confirmed the eutectic temperature involving forsterite and magnesia, but the wide solubility of SiO_2 in MgO (10 mol% at 1863 °C) which they reported is in contradiction with other investigations. For example, Henriksen and Kingery [14] found a solubility of SiO_2 in MgO less than 0.34 mol% at 1850 °C.

The chemical activities of MgO and SiO_2 have been experimentally determined by various authors using high-temperature mass spectrometry. Kambayashi and Kato [15,16] measured the activities at 1600 and 1700 °C and determined the standard Gibbs free energies of formation of MgSiO_3 and Mg_2SiO_4 from $\text{SiO}_2(\text{s})$ and $\text{MgO}(\text{s})$ at 1600 °C. Richardson [17] investigated the activities of MgO and SiO_2 in the liquid at 1600 °C. Rein and Chipman reported calculated activities of SiO_2 and MgO, which were estimated from the silicon distribution between slag and Fe–Si–C alloys (SiO_2) and by using the Gibbs–Duhem relationship (MgO) [18]. Stolyarova et al. [19] measured both activities at 1497 °C and 1617 °C and determined the Gibbs free energy of formation and the excess Gibbs free energy of formation in the MgO– SiO_2 system. Zaitsev and Arutyunyan [20,21] studied the activities by Knudsen mass spectrometry over a wide temperature range (1300–1600 °C) and determined the temperature dependence of the standard Gibbs free energies of formation of magnesium silicates.

A detailed study of the phase equilibria in the ternary system K_2O –MgO– SiO_2 has been made by Roedder [3,4] using the quenching method for the silica-rich composition range. The stability fields of the various crystalline phases have been derived. Four compounds have been found and their thermal relationships have been determined. The compound K_2MgSiO_4 melts congruently at approximately 1650 °C. However, the precise determination of the melting behaviour was complicated due to high losses of potash during the experiment. Regarding the structure of the compound it was mentioned that it could be considered as cubic phase like $\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3$ if the substitution $2\text{Al}^{3+} \leftrightarrow \text{Mg}^{2+} + \text{Si}^{4+}$ is supposed. The solid solution between Mg_2SiO_4 and K_2MgSiO_4 was not confirmed [22].

Temperatures of 1134 ± 1 °C and 1089 ± 1 °C, respectively, have been estimated for the congruent melting points of the compounds $\text{K}_2\text{MgSi}_3\text{O}_8$ and $\text{K}_2\text{MgSi}_5\text{O}_{12}$, correspondingly. The X-ray data on the compound $\text{K}_2\text{MgSi}_3\text{O}_8$ indicate a solid–solid phase transition that could however not be detected by the DTA analysis and was not conclusively confirmed optically [3,4]. Taking into account the substitution mentioned above, the assumption of a structural similarity of $\text{K}_2\text{MgSi}_3\text{O}_8$ and $\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$, which is known as natural or synthetic kaliophilite or kalsilite, could be made but the differences in crystallographic properties were found to be too large and could not be related to the possible inaccuracy in measuring $\text{K}_2\text{MgSi}_3\text{O}_8$.

According to Roedder $\text{K}_2\text{MgSi}_5\text{O}_{12}$ occurs in two modifications, an isotropic and an anisotropic form, derived from optical properties of crystals. The isotropic form seemed to crystallise first, and, if sufficient time is allowed in the furnace, it slowly converted into the anisotropic form, regardless of the temperature. The detailed investigations were difficult due to the slow reaction of crystallisation from the glass. Thus, the transformation temperature has not been estimated. The DTA analysis has not shown any thermal activity from 20 to 1089 °C, while crystallographic data obtained

using XRD indicated two modifications [4]. The nature of the transformation regarding the compound $\text{K}_2\text{MgSi}_5\text{O}_{12}$ was reported to be similar to that of $\text{K}_2\text{MgSi}_3\text{O}_8$. If Al_2O_3 is substituted for MgO and SiO_2 in the compound $\text{K}_2\text{MgSi}_5\text{O}_{12}$, the end result would be leucite $\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2$, for which the transformation is well-known. The available crystallographic data allow the assumption that $\text{K}_2\text{MgSi}_5\text{O}_{12}$ could be considered as a leucite analogue where a coupled substitution is observed: $2\text{Al}^{3+} \leftrightarrow \text{Mg}^{2+} + \text{Si}^{4+}$. As an indirect argument to the structural similarity, Schairer [23] has mentioned the complete series of the solid solution between leucite and $\text{K}_2\text{MgSi}_5\text{O}_{12}$.

The nature of the polymorphism between disordered and ordered samples has been discussed relative to the different synthesis conditions [24,25]. The dry synthesised sample revealed cubic structure with random distribution of atoms on tetrahedron sites. Under hydrothermal conditions the sample is probably monoclinic with ordered Si and Mg on the T-sites [25]. Ignoring T-site ordering, the two structures are topologically identical. Water in the hydrothermal synthesis accelerates Si–Mg ordering, allowing the thermodynamically more stable phase to be formed [24].

The elastic cubic–tetragonal phase transition in leucite, which is considered as analogue of $\text{K}_2\text{MgSi}_5\text{O}_{12}$ is independent of Al/Si ordering in the framework. If the exchange interaction for ordering is modified by chemical substitution of Al by a larger cation such as Mg, the local strain associated with low temperature disorder is enhanced and the ordered polymorphs are stabilized. The elastic shear transformation in $\text{K}_2\text{MgSi}_5\text{O}_{12}$ is expected to be strongly dependent on tetrahedral site ordering [26]. Later Redfern [27] has estimated the first-order ferroelastic transition [28] between room-temperature and high-temperature phase of $\text{K}_2\text{MgSi}_5\text{O}_{12}$ at 349 °C. The spontaneous strain behaves as the order parameter for the transition.

A further compound $\text{K}_2\text{Mg}_5\text{Si}_{12}\text{O}_{30}$, called Roedderite in the literature, has been reported to melt incongruently at 1174 ± 2 °C to form MgSiO_3 and liquid. It shows as a very small field in the liquidus surface [3,4]. Its composition has been confirmed by Khan [29] who has synthesised the compound and studied it by electron microscope analysis.

Three of the ternary compounds reported by Roedder fall on the central line starting from silica to the composition “ K_2O : MgO=1:1”. This section has been investigated later by Roth [30], who has considered the section between K_2MgSiO_4 and silica among a large number of subsystems in the whole system K_2O –MgO– Fe_2O_3 – Al_2O_3 – SiO_2 . The phase diagram [30] has a good correlation with the data of Roedder [3,4], especially in the concentration range of high silica, but two additional compounds with compositions $\text{K}_{10}\text{Mg}_5\text{Si}_{11}\text{O}_{32}$ and $\text{K}_4\text{Mg}_2\text{Si}_5\text{O}_{14}$ have been introduced along with the proposed solubility of SiO_2 in K_2MgSiO_4 .

The phases on the line K_2MgSiO_4 to silica can be considered essentially isostructural with those on the join KAlO_2 – SiO_2 . A structural substitution of $2\text{Al} \leftrightarrow \text{MgSi}$ can take place, so that a compound is formed isostructural with KAlO_2 at the composition $\text{K}\{\text{Mg}_{0.5}\text{Si}_{0.5}\}\text{O}_2$ or K_2MgSiO_4 .

All kalsilite-like phases from the section K_2MgSiO_4 – SiO_2 ($\text{K}_2\text{MgSi}_3\text{O}_8$, $\text{K}_4\text{Mg}_2\text{Si}_5\text{O}_{14}$, $\text{K}_{10}\text{Mg}_5\text{Si}_{11}\text{O}_{32}$) are reported by Roth to exist as solid solutions with small ranges of solubility. The compound $\text{K}_2\text{MgSi}_3\text{O}_8$ has two modifications, monoclinic at high and hexagonal at low temperature. According to Roth [30], this compound does not melt congruently as suggested in the work of Roedder, but decomposes into liquid and a phase deficient in silica with composition $\text{K}_4\text{Mg}_2\text{Si}_5\text{O}_{14}$. For the latter Roth suggested a limiting case behaviour (see also Fig. 3) similar to the melting of mullite. The crystal structure of this phase has been refined in a later work by Dollase [31]. The tetragonal phase like $\text{K}_{10}\text{Mg}_5\text{Si}_{11}\text{O}_{32}$ has been reported first by Cook et al. [32] in both systems KAlO_2 – SiO_2 and KFeO_2 – SiO_2 . The phase occurs in the K_2MgSiO_4 – SiO_2

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