Shornikov S.I., Archakov I.Yu. Investigation of thermodynamic properties of solid phases in the system Al$_2$O$_3$-SiO$_2$ using the mass-spectrometry
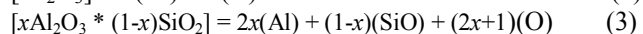
Grebenshchikov's Institute of Chemistry of Silicates, Russian Academy of Science, 199155 St.-Petersburg, ul. Odoevskogo, 24-2, Russia, e-mail: arch@ipme.ru

key words: thermodynamics of silicates, the system Al$_2$O$_3$-SiO$_2$, Knudsen mass-spectrometry.

The system Al$_2$O$_3$-SiO$_2$ is interesting for different technological processes. It is known that at high temperatures, phase relations and thermodynamics of the system Al$_2$O$_3$-SiO$_2$ are determined mostly by properties of mullite, the only stable compound in the system. A problem of the mullite formula and the boundaries of its stability is not fully solved. There are data both on presence and absence of solid solutions between mullite and corundum and silica.

The purpose of the present study was an investigation of thermodynamic properties of solid phases in the system Al$_2$O$_3$-SiO$_2$, accented on the data on the sub-solidus region. The experimental data were obtained using the Knudsen mass-spectrometric effusive method in the temperature range 1676 – 2327 K by vaporization of samples from molybdenum chambers. Conditions of the runs and synthesis of the samples in the system Al$_2$O$_3$-SiO$_2$, as well as characteristics of used equipment are described in [1].

As it is shown in [2], significant changes of a composition of a condensed phase occur during vaporization of melts in the system Al$_2$O$_3$-SiO$_2$ because of different rates of vaporization of different components. For vaporization of samples in the sub-solidus of the system Al$_2$O$_3$-SiO$_2$ and the regions of crystal-melt equilibria, lower rates of vaporization are characteristic. Therefore, composition of the samples does not changes during the experiments. Heterogeneous reactions corresponding to the vaporization can be written

$$[SiO_2] = (SiO) + (O) \tag{1}$$
$$[Al_2O_3] = 2(Al) + 3(O) \tag{2}$$
$$[xAl_2O_3 * (1-x)SiO_2] = 2x(Al) + (1-x)(SiO) + (2x+1)(O) \tag{3}$$

where x – relative content of aluminum oxide in mullite, rounded parenthesizes correspond to vapor components, square parenthesizes correspond to solid components.
Partial pressures of vapor (p(i)) of gaseous components of reactions (1)-(3), i.e. (SiO), (Al), (O), were calculated by the Hertz-Knudsen equation, assuming equal partial coefficients of the mullite vaporization and partial coefficients of the silica and alumina vaporization.

Obtained values of p^*(SiO) and p^*(O) within the *S-M* compositional interval (A = Al$_2$O$_3$, S = SiO$_2$, M = mullite) are equal to those over pure silica (Fig.1a), whereas values of p^*(Al) and p^*(O) over the system Al$_2$O$_3$-SiO$_2$ in the *M-A* compositional interval are equal to p^O(Al) and p^O(O) over pure alumina (symbols *, ** , and ^{O} correspond to *S-M, M-A* compositional regions and pure silica and alumina).

Insignificant change of an inclination of a thermal dependence of p*(SiO) in the interval 1950-2180 K (Fig. 1b) corresponds to enthalpy of transition from the *M+S* region to the *M*+liquid region. Corresponding change in the inclination of p*(Al) and p*(O) is unrecognizable (Figs. 1b, c).

Estimation of a maximal enthalpy of this transition and the transition from the *M+S* region into the *S*+liquid region is insignificant with respect to melting enthalpies and does not exceed 5 kJ/mol. A change of the inclination of a thermal dependence of p*(SiO) in the *A*+liquid region (Fig. 1a) is determined by enthalpy of transition from the *M+A* region into the *A*+liquid region. Calculation of this value is difficult because of method discrepancies. Enthalpy of this transition is estimated as 13±10 kJ/mol.

(a)
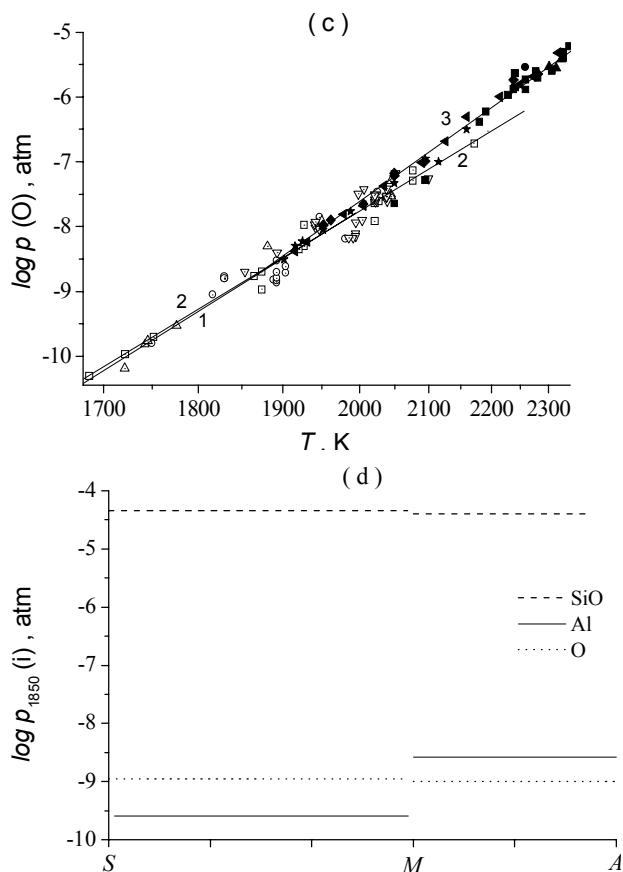

(b)
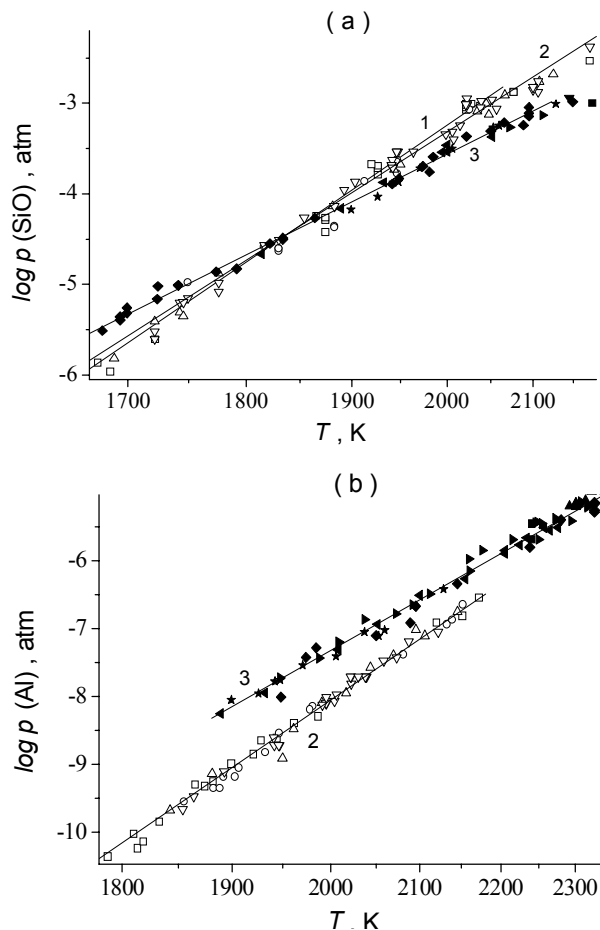
Fig.1. Thermal (a-c) and compositional (d) dependences of partial vapor pressure of (SiO), (Al), and (O) over the system Al_2O_3-SiO_2. Open symbols show the results within the interval *S-M*, filled symbols show the results within the interval *M-A*. Lines denote the thermal dependence $p(i)$ over silica (1), over interval *S-M* (2), over interval *M-A* (3), and over alumina (4).

thalpies of some phase transitions showed that their maximal values were insignificant in comparison to the enthalpy effects of melting. The observed regularities of thermal-compositional dependences of partial pressures of components, prevailing in vapor over the system within the intervals silica-mullite and mullite-alumina, confirm the mullite composition, $3Al_2O_3 \cdot 2SiO_2$. Taking into account the experimental errors, the formation of solid solutions and additional compounds in the system Al_2O_3-SiO_2, besides stoicheometric mullite (at high temperature), is not confirmed.

References:

1. Shornikov S.I., Archakov I.Yu., Chemekova T.Yu. // J. Phys. Chem. 2000. V. 74, 5, P. 775-782.
2. Shornikov S.I., Archakov I.Yu. // J. Phys. Chem. 2000. V. 74, 5, P. 783-788.
3. McHall J.M., Yuerekli K., Dabbs D.M., Navrotsky A., Sundaresan S., Aksay I.A. // Chem. Mater. 1997. V.9. P. 3096-3100.
4. Horibe T., Kuwabara S. // Bull. Chem. Soc. Japan. 1967. V. 40. P. 972-982.
5. Barta R.R., Barta Ch.R. // J. Applied Chem. 1956. T. 29. P. 341-353.
6. Toropov N.A., Galakhov F. Ya. // Isv. AN SSSR. Otd. Khim. Nauk. 1958. P. 8-11.

Fig. 1d shows that the obtained values of partial vapor pressure of (SiO), (Al), and (O) in the sub-solidus of the system are constant in each of compositional ranges *S-M* and *M-A*. Values of partial pressure $p(SiO)$ and $p(O)$ in the interval *S-M* are slightly higher, than in the interval *M-A*. An opposite dependence is observed for $p(Al)$. The observed character of the compositional dependences of partial vapor pressure corresponds also to insignificant energetic effects of solid-state transformations in comparison to the values for melts in the system Al_2O_3-SiO_2. Within the experimental accuracy, the stability of solid solutions [3-5] is not confirmed.

Taking into account an equality of equilibrium constants for reaction (3), related to different compositional intervals of the system, i.e. *S-M* and *M-A*, both Gibbs energy of mullite formation from oxides ($\Delta_f G_T$) and formula of mullite can be deduced by solution of the following equations

$$\Delta_f G_T(M) = xRT\left(2\ln\frac{p^*(Al)}{p^{**}(Al)} + 3\ln\frac{p^*(O)}{p^{**}(O)}\right) \quad (4)$$

$$\Delta_f G_T(M) = (1-x)RT\left(\ln\frac{p^{**}(SiO)p^{**}(O)}{p^*(SiO)p^*(O)}\right) \quad (5)$$

The obtained value x corresponds to the formula of stoicheometric mullite, containing 60±5 mo. % Al_2O_3, that is in agreement with [6].

Thus, thermodynamic properties of the sub-solidus of the system Al_2O_3-SiO_2 are firstly studied by the Knudsen effusive mass-spectrometry method. Estimations of en-