Vapor Formation and the Thermodynamic Properties of the SrO—Al₂O₃—SiO₂ System

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**Abstract**—Vaporization and thermodynamic properties of the SrO—Al₂O₃—SiO₂ system are studied by high-temperature differential mass spectrometry in the concentration range from 90 to 10 mol % of SrO and the molar ratio of \(x(\text{Al}_2\text{O}_3)/x(\text{SiO}_2) = 1.5\). The samples are evaporated from Knudsen effusion chambers made of tungsten. The partial pressures of the molecular forms of the vapor, the activities of the condensed phase components, the Gibbs energies, and the excess Gibbs energies are determined. It is established that the studied system is characterized by a slight negative deviation from the ideal behavior. For mullite (Al₆Si₂O₁₃) the value of the standard enthalpy of formation is determined. The melting points of the synthesized samples are established by high-temperature microscopy.

**Keywords:** vaporization, thermodynamic properties, SrO—Al₂O₃—SiO₂, high-temperature mass spectrometry, vaporization, oxides of strontium, aluminum and silicon, activity, Gibbs energy, melting points

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**INTRODUCTION**

The development of aviation and space technology requires the development of new materials with specific physical and chemical properties. When designing aircraft, one should first of all take into account the fact that parts of aircraft and spacecraft will be exposed to extremely high temperatures during operation. The efficiency of using various aerospace systems is largely determined by the characteristics of the radio engineering devices placed onboard [1]. To protect these devices from external influences, various radiotransparent materials with sufficiently high thermal stability are used. Glass ceramics based on aluminosilicate systems are used as such materials. In recent years, researchers have paid increased attention to materials based on SrO—Al₂O₃—SiO₂ (SAS) and BaO—Al₂O₃—SiO₂ (BAS) systems, which have high melting points, thermal stability, and good strength properties, which make them promising for the fabrication of radiotransparent materials [2—4]. Composite materials based on SAS and BAS have high resistance to thermal shock, high chemical resistance, and stable dielectric properties, which make these materials suitable for manufacturing high-temperature antenna radomes and radio-transparent windows of high-speed aircraft with an operating temperature of at least 2300 K.

During the operation of radiotransparent ceramics at high temperatures, processes of selective evaporation of more volatile components may occur, leading to an irreversible change in specific properties. In relation to this, one of the main tasks is to experimentally study the vaporization and thermodynamic properties of glass-ceramic radiotransparent materials in order to identify compositions with the maximum thermal stability.

The most volatile components in the SrO—Al₂O₃—SiO₂ system are strontium oxide and silicon dioxide [5], which begin to transform into vapor at temperatures on the order of 1900 to 2000 K. The formation of solid solutions and thermally stable compounds in SrO—Al₂O₃ [6—8], SrO—SiO₂ [9—11], and Al₂O₃—SiO₂ [12—27] binary systems, as well as in the SrO—Al₂O₃—SiO₂ ternary system [28—30], reduces the activity of the condensed phase components and increases the vaporization temperature. Figure 1 shows a diagram of the triangles of coexisting phases in the subsolidus region and Fig. 2 contains the melting diagram of the SrO—Al₂O₃—SiO₂ system.

**EXPERIMENTAL**

The vaporization processes and thermodynamic properties of the SrO—Al₂O₃—SiO₂ were studied by high-temperature mass spectrometry on an MS-1301
Fig. 1. Triangle diagram of coexisting phases of the SrO–Al₂O₃–SiO₂ system in the subsolidus region at a temperature of 1623 K [31].

Fig. 2. Melting diagram of the SrO–Al₂O₃–SiO₂ system [32].
mass spectrometer (SKB of Analytical Instrumentation of the Academy of Sciences of the USSR, Leningrad) at an energy of ionizing electrons of 30 eV. The studied samples were evaporated from a double single-temperature Knudsen chamber made of tungsten. A sample was loaded into one of the cells of the chamber, and oxides of strontium or silicon alternately were loaded into the other, comparative cell. The chamber was heated by electron bombardment, and the temperature was measured with an EOP-66 optical pyrometer. The equipment was preliminarily calibrated against the vapor pressure of CaF₂ [33].

In this study, in the SrO–Al₂O₃–SiO₂ system, ten samples were synthesized by solid-phase synthesis (SPS), whose compositions lie on the secant phase diagram of the SrO–Al₂O₃–SiO₂ system (Figs. 1 and 2) [31, 32]. The chemical composition of the samples (by synthesis) is indicated in Figs. 1 and 2 by points and is presented in Table 1. The point numbers in Figs. 1 and 2 correspond to the sample numbers in Table 1. In the synthesis, SrCO₃, Al₂O₃, and crystalline SiO₂ were used as the initial reagents. All reagents were of analytical grade. For homogenization, the sample was ground in a Retsch PM 100 planetary ball mill for 2 h and pressed into tablets 1 cm in diameter in a hydraulic press at a pressure of 4 tons. The obtained tablets were calcined in a Nabertherm Top 16/R muffle furnace in corundum crucibles at 1523 K for 12 h. The samples were cooled together with the furnace. Next, the samples were crushed in an agate mortar and their X-ray phase analysis was carried out to control the achievement of equilibrium by the samples. If the equilibrium phase composition was not achieved, repeated calcination was carried out under the same conditions.

The degree of interaction of the initial reagents in the synthesized samples was controlled by X-ray phase analysis (XPA) on a DRON-3M diffractometer using CuKα radiation. The measurements were carried out in a continuous mode at the 2θ diffraction angles in the range from 10° to 70° at a scanning rate of 2°/min. The crystalline phases were identified using the PDF-2 powder diffraction database.

The X-ray diffraction patterns of the synthesized ceramic samples in the SrO–Al₂O₃–SiO₂ system with the identification of crystalline phases are presented in Figs. 3 and 4.

Table 2 shows the phase composition of the samples in the SrO–Al₂O₃–SiO₂ system after isothermal holding for 12 h and 24 h at an SPS temperature of 1523 K, and also the melting points of the obtained samples measured on a high-temperature microscope (HTM), whose design was developed at the Institute of Chemical Chemistry of the Russian Academy of Sciences [34]. The temperature determination error was ±20 K.

The XPA data (Figs. 3, 4, Table 2) show the formation in sample nos. 1–8 of at least two clearly fixed phases that satisfactorily correspond to the triangulation presented in Fig. 1. Sample no. 8, in which the crystalline compound Sr₄Al₂O₇, absent in the SrO–Al₂O₃–SiO₂ phase diagram, according to [31], but present in the PDF-2 database and on the phase diagram of the ternary system in [35], is an exception. The third phase cannot be determined precisely because of its low content in the samples and numerous overlapping peaks.

Comparison of the phase composition of the samples obtained during isothermal exposure for 12 and 24 h at a temperature of 1523 K shows that the phase equilibrium is achieved either in 12 h or not at all, as is the case in sample nos. 9 and 10. Sample no. 10 has a stoichiometric composition corresponding to mullite (3Al₂O₃·2SiO₂); however, even after daily heat treatment, there are no signs of the formation of mullite in it. The sample remains the same mixture of quartz and corundum as its original charge. Sample no. 9, containing in the original composition 90 mol % SrO, upon subsequent storage in air, interacts with moisture, forming hydroxide Sr(OH)₂, which is recorded in sample no. 9 during X-ray photography. In addition to strontium hydroxide, this sample also contains quartz. The X-ray diffraction patterns of sample no. 9, kept for 12 and 24 h at a temperature of 1523 K, are almost identical; no interaction between the components is detected. In sample no. 8, after 12 hours of exposure at a temperature of 1523 K, together with silicate and strontium aluminate (Table 2), its hydroxide Sr(OH)₂ is also recorded, which indicates the presence of residual, unreacted SrO in the hot sample. After increasing the isothermal exposure to 24 h, strontium oxide completely reacts with the formation of aluminate and silicate, and traces of strontium hydroxide are no longer detected on the X-ray diffraction pattern of the cold sample no. 8 (Fig. 4). Thus, we observe the reduced reactivity of oxides not only in sample no. 10, which
does not contain SrO, but also in sample no. 9, which contains a significant excess of it. In the mass spectra of vapor over the studied samples in the temperature range 1950–2010 K, peaks of Sr\(^+\) and SiO\(^+\) ions were recorded, whose intensity ratio at a fixed temperature depended on the initial composition of the sample. During isothermal holding, the intensity of ion currents of Sr\(^+\) and SiO\(^+\) gradually decreased. In the mass spectra of vapor over sample nos. 1–3 and 10, ions WO\(_2^+\) and WO\(_3^+\), formed during the ionization of the corresponding molecules, which are the result of the interaction of samples with the material of the effusion chamber, were recorded. To search for molecular precursors of Sr\(^+\) and SiO\(^+\) ions, the energies at which they occurred were measured by the vanishing ion current method [36]. The obtained values 5.8 ± 0.3 and 11.5 ± 0.3 eV, respectively, coincide with the ionization energies of atomic strontium and silicon monoxide [37]. As the temperature increased to 2250 K, Al\(^+\), AlO\(^+\), and Al\(_2\)O\(^+\) ions appeared in the mass spectra of the vapor at energies of their occurrence of 6.1, 9.6, and 7.9 eV, respectively. An analysis of the mass spectra of the vapor over the
studied samples and the energies of the appearance of ions in the mass spectra of the vapor indicate that, in the temperature range of 1950 to 2010 K, SiO, atomic strontium, and oxygen pass into the vapor according to equations of reactions (1) and (2).

\[
\text{SrO} \rightarrow \text{Sr} + \text{O}, \quad (1)
\]
\[
\text{SiO}_2 \rightarrow \text{SiO} + \text{O}, \quad (2)
\]

In this case, aluminium accumulates in the condensed phase, which passes into vapor at a higher temperature according to Eqs. (3–5).

\[
\text{Al}_2\text{O}_3(s, l) = 2\text{Al}(g) + 3\text{O}(g), \quad (3)
\]
\[
\text{Al}_2\text{O}_{3}(s, l) = 2\text{AlO}(g) + \text{O}(g), \quad (4)
\]
\[
\text{Al}_2\text{O}_3(s, l) = \text{Al}_2\text{O}(g) + 2\text{O}(g). \quad (5)
\]

The partial pressures of atomic strontium and SiO were determined by comparing ion currents [36] using Eqs. (6) and (7), respectively.

\[
p(\text{Sr}) = p_0(\text{Sr}) \frac{I(\text{Sr}^+)}{I_0(\text{Sr}^+)}. \quad (6)
\]
\[
p(\text{SiO}) = p_0(\text{SiO}) \frac{I(\text{SiO}^+)}{I_0(\text{SiO}^+)}. \quad (7)
\]

Here \( p \) and \( p_0 \) are partial vapor pressures above the sample and pressure standard, and \( I \) and \( I_0 \) are the intensities of ion currents in the mass spectra of the vapor above the sample and the standard. Quantities \( p_0 \) were calculated by Eqs. (8) [8] and (9) [27], respectively.

\[
\lg p(\text{Sr}, \text{Pa}) = -21839 \pm 547 + (11.35 \pm 0.30), \quad (8)
\]
\[
\lg p(\text{SiO}, \text{Pa}) = -24676 \pm 552 + (13.07 \pm 0.01). \quad (9)
\]

The partial pressure of oxygen was not experimentally measured for a number of reasons. In particular, molecular beams of atomic and molecular oxygen repeatedly fly through the ionization region without condensing on the cold parts of the mass spectrometer. This significantly distorts the quantitative characteristics. In addition, oxygen is present in the residual gases of the mass spectrometer. Oxygen escaping from the Knudsen chamber is not blocked by the mass spec-

Table 2. Phase composition of samples in the SrO–Al2O3–SiO2 system after exposure at a temperature of 1523 K for 12 and 24 h and their melting points (\( T_{\text{melt}} \)) according to the HTM.

<table>
<thead>
<tr>
<th>N</th>
<th>SrO</th>
<th>Al2O3</th>
<th>SiO2</th>
<th>( T_{\text{melt}} ) K</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10</td>
<td>54</td>
<td>36</td>
<td>1848</td>
</tr>
<tr>
<td>2</td>
<td>20</td>
<td>48</td>
<td>32</td>
<td>1858</td>
</tr>
<tr>
<td>3</td>
<td>30</td>
<td>42</td>
<td>28</td>
<td>1833</td>
</tr>
<tr>
<td>4</td>
<td>40</td>
<td>36</td>
<td>24</td>
<td>1815</td>
</tr>
<tr>
<td>5</td>
<td>50</td>
<td>30</td>
<td>20</td>
<td>1843</td>
</tr>
<tr>
<td>6</td>
<td>60</td>
<td>24</td>
<td>16</td>
<td>1929</td>
</tr>
<tr>
<td>7</td>
<td>70</td>
<td>18</td>
<td>12</td>
<td>1913</td>
</tr>
<tr>
<td>8</td>
<td>80</td>
<td>12</td>
<td>8</td>
<td>1898</td>
</tr>
<tr>
<td>9</td>
<td>90</td>
<td>6</td>
<td>4</td>
<td>–</td>
</tr>
<tr>
<td>10</td>
<td>0</td>
<td>60</td>
<td>40</td>
<td>–</td>
</tr>
</tbody>
</table>

\( \text{Mol} \% \)
The partial pressure of atomic oxygen was calculated using Eq. (10) [38].

\[
p(O) = p(Sr) \frac{M(O)}{M(Sr)} + p(SiO) \frac{M(O)}{M(SiO)},
\]

(10)

where \(M\) is the molecular weight of the corresponding particle. The use of a double single-temperature Knudsen chamber made it possible to determine the activities of SrO and SiO\(_2\) in the condensed phase according to Eqs. (11) and (12).

\[
a(SrO) = \frac{p(SrO)}{p_0(SrO)} = \frac{p(Sr)}{p_0(Sr)} \frac{p(O)}{p_0(O)} = \frac{p^2(Sr)}{p_0^2(Sr)},
\]

(11)

\[
a(O_2) = \frac{p(SiO_2)}{p_0(SiO_2)} = \frac{p(SiO)}{p_0(SiO)} \frac{p(O)}{p_0(O)} = \frac{p^2(SiO)}{p_0^2(SiO)}.
\]

(12)

At a temperature of 2000 K, sample nos. 1–8, according to the phase diagram of the SrO–Al\(_2\)O\(_3\)–SiO\(_2\) system [28, 39] belong to the region of a homogeneous melt. This made it possible to determine the activity of aluminum oxide using the Gibbs–Duhem equation, presented for this system in differential (13) and integral (14) forms. Integration was performed by a graphical method with extrapolation to infinite dilution [40].

\[
x(SrO) \ln a(SrO) + x(Al_2O_3) \ln a(Al_2O_3) + x(SiO_2) \ln a(SiO_2) = 0,
\]

(13)

\[
\ln a(Al_2O_3) = - \int \frac{x(SrO)}{x(Al_2O_3)} d \ln a(SrO) - \int \frac{x(SiO_2)}{x(Al_2O_3)} d \ln a(SiO_2).
\]

(14)

The values of the activities of all track components of the condensed phase obtained for sample nos. 1–7 made it possible to determine the values of the Gibbs energies and excess Gibbs energies using Eqs. (15) and (16), respectively.

\[
G = \sum x_i \ln a_i,
\]

(15)

\[
G^E = \sum x_i \ln \gamma_i.
\]

(16)

Here \(x_i\) is the mole fraction of the \(i\)th component of the melt, \(a_i\) is the value of the activity of the \(i\)th component, and \(\gamma_i\) is the activity coefficient of the \(i\)th component. The data obtained are presented in Table 3.

### RESULTS AND DISCUSSION

According to the data presented in Table 2, the phase composition of the samples is practically independent of the duration of isothermal exposure at a temperature of 1523 K. The only case of detecting a difference in the phase composition of the samples after 12 and 24 h of exposure at a temperature of 1523 K is related to sample no. 3 (Table 2). After 12 h of heat treatment, a mixture of two phases of Sr\(_6\)Al\(_{18}\)Si\(_2\)O\(_{37}\) + Sr\(_2\)Al\(_2\)Si\(_6\)O\(_{19}\), and after 24 h a mixture of Sr\(_6\)Al\(_{18}\)Si\(_2\)O\(_{37}\) + Sr\(_5\)Al\(_2\)Si\(_2\)O\(_8\), are recorded. Thus, with an increase in the heat treatment time, an aluminosilicate is formed with

### Table 3. Partial pressures of molecular forms of vapor over the studied samples of the SrO–Al\(_2\)O\(_3\)–SiO\(_2\) system, values of the activities of the components of the condensed phase, and the Gibbs energies and excess Gibbs energies at a temperature of 2000 K

<table>
<thead>
<tr>
<th>Sample no.</th>
<th>Sample composition, mol %</th>
<th>(p_i), Pa</th>
<th>(a_i)</th>
<th>(\Delta G(T)), kJ</th>
<th>(\Delta G^E(T)), kJ</th>
</tr>
</thead>
<tbody>
<tr>
<td>SrO</td>
<td>Al(_2)O(_3)</td>
<td>SiO(_2)</td>
<td>Sr</td>
<td>SiO</td>
<td>O</td>
</tr>
<tr>
<td>0</td>
<td>60</td>
<td>40</td>
<td>3.45</td>
<td>2.07</td>
<td>0</td>
</tr>
<tr>
<td>1</td>
<td>10</td>
<td>54</td>
<td>36</td>
<td>4.7 × 10(^{-3})</td>
<td>2.96</td>
</tr>
<tr>
<td>2</td>
<td>20</td>
<td>48</td>
<td>32</td>
<td>7.9 × 10(^{-3})</td>
<td>2.16</td>
</tr>
<tr>
<td>3</td>
<td>30</td>
<td>42</td>
<td>28</td>
<td>1.5 × 10(^{-2})</td>
<td>1.91</td>
</tr>
<tr>
<td>4</td>
<td>40</td>
<td>36</td>
<td>24</td>
<td>6.1 × 10(^{-2})</td>
<td>1.40</td>
</tr>
<tr>
<td>5</td>
<td>50</td>
<td>30</td>
<td>20</td>
<td>9.3 × 10(^{-2})</td>
<td>0.64</td>
</tr>
<tr>
<td>6</td>
<td>60</td>
<td>24</td>
<td>16</td>
<td>0.12</td>
<td>0.50</td>
</tr>
<tr>
<td>7</td>
<td>70</td>
<td>18</td>
<td>12</td>
<td>0.93</td>
<td>0.19</td>
</tr>
<tr>
<td>8</td>
<td>80</td>
<td>12</td>
<td>8</td>
<td>1.96</td>
<td>—</td>
</tr>
<tr>
<td>9</td>
<td>90</td>
<td>6</td>
<td>4</td>
<td>2.69</td>
<td>—</td>
</tr>
</tbody>
</table>
a lower content of strontium and with a higher content of silica.

As mentioned above, in sample no. 10, after daily heat treatment, mullite is not formed, and the sample remains a mixture of quartz and corundum, like the original charge. According to [41], Al2O3 and SiO2 have a low reactivity capability, which makes direct solid-phase synthesis difficult and requires a significant increase in the firing temperature. The synthesis of single-phase mullite is associated with significant difficulties, mainly due to the low diffusion mobility of aluminum cations and silicon through the layer of mullite formed at the boundary between the particles of the original oxides. Even prolonged firing of the reaction mixture at elevated temperatures does not allow the reaction to be completed. Mullite is formed from pure silicon and aluminum oxides at a temperature of about 1873 K [42]. Since the vaporization of the 3Al2O3–2SiO2 system was studied at a higher temperature, the mullite was formed directly in the effusion chamber. This is indicated by the decrease in the activity of SiO2 from 1 to 0.41 and the enthalpy of reaction (13) determined by us, which, within the permissible error, coincides with the reference data [43]. Determination of the temperature dependence of the SiO+ ion current intensity in the mass spectrum of the vapor over sample No. 10 (Al2SiO3 mullite), made it possible to obtain the equation for the dependence of the partial pressure of SiO on temperature (17) in the temperature range 1871–2053 K and determine the enthalpy of reaction (18) at a temperature of 1995 K equal to 2108 ± 155 kJ.

\[
\lg p(\text{SiO}, \text{Pa}) = -\frac{27526 \pm 2046}{T} + (12.610.96), \quad (17)
\]

\[
\text{Al}_6\text{Si}_2\text{O}_{13} \text{(cr)} = 3\text{Al}_2\text{O}_3 \text{(cr)} + 2\text{SiO} \text{(g)} + 2\text{O}_2 \text{(g)}. \quad (18)
\]

The experimental data we obtained on determining the values of the activity of the components of the condensed phase indicate that the system studied by us is characterized by a negative deviation from the ideal behavior. This is due to the fact that the SrO–Al2O3–SiO2 system is formed by oxides that differ in their acid-base properties. Strontium oxide is a typical basic oxide and forms thermally stable compounds with amphoteric aluminum oxide and acidic silica. In particular, aluminum oxide forms Al2SiO3 with silicon dioxide mullite, and in the SrO–Al2O3–SiO2 system, according to the data of [28], there are three-component compounds: anorthite, (SrAl2Si2O8), gehlenite (Sr2Al2Si2O7), and Sr4Al10Si2O37.

When strontium oxide interacts with the chamber’s material, gaseous strontium tungstates can be formed [44]. The absence in the mass spectra of vapor over the studied samples of the SrWO5+ and SrWO3+ ions appears to be related to the low partial pressures of SrO and tungsten oxides.

The enthalpy of reaction (18) recalculated to a temperature of 298 K using the reference data [43] was 2143 ± 158 kJ. The value of the enthalpy of the formation of mullite from oxides at a temperature of 1995 K is −96 ± 160 kJ/mol, and at a temperature of 298 K, it is −20 ± 160 kJ/mol. The enthalpy of the formation of mullite determined in this work, of −6869 ± 160 kJ/mol, agrees well with the value of −6819.2 kJ/mol given in the reference book [43]. The obtained values of the activities of silicon and aluminum oxides for sample no. 10, which corresponds to the composition of mullite, differ from the data presented in [16, 21–23]. In our opinion, the activity of Al2O3, determined in these works, and equal to unity, does not refer to the Al6Si2O13 compound, but to the region of the phase diagram of Al6Si2O13 + Al2O3. The region of the existence of mullite is quite narrow; thus, the transition from Al6Si2O13 to Al6Si2O13 + Al2O3 at high temperatures occurs quite quickly due to the predominant removal of silicon oxide from the system.

CONCLUSIONS

The processes of vaporization of the SrO–Al2O3–SiO2 system were studied by high-temperature differential mass spectrometry at a temperature of 2000 K in the concentration range from 90 to 10 mol % SrO and the molar ratio X(Al2O3)/X(SiO2) of 1.5. The samples were synthesized by solid-phase synthesis from analytical grade SrCO3, Al2O3, and SiO2. The samples were identified by X-ray phase analysis. It has been established that an increase in the heat treatment time from 12 to 24 h at a temperature of 1523 K does not lead to a significant change in the phase composition for most samples. The melting temperatures of the synthesized samples, which lie in the range 1815–1929 K, were determined by high-temperature microscopy. It was shown that the difference in the volatility of the oxides forming the system leads to the selective evaporation of strontium and silicon oxides and the accumulation of aluminum oxide in the condensed phase. The application of the method of differential high-temperature mass spectrometry using individual oxides of strontium and silicon as standards makes it possible to determine the values of the activities of SrO and SiO2 at a temperature of 2000 K in the entire concentration range of compositions. For a region of a homogeneous melt, using the Gibbs–Duhem equation, the activity values of aluminum oxide were calculated and the Gibbs energies and excess Gibbs energies were determined. It is established that the studied system is characterized by the negative deviation from the ideal behavior. For mullite (Al6Si2O13), the standard enthalpy of formation was determined to be −6869 ± 160 kJ/mol.


