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Thermodynamic Properties of Silicate Glasses and Melts: II.[1] System $SrO–SiO_2$

S. I. Lopatin[a], S. M. Shugurov[a], V. L. Stolyarova[a], and N. G. Tyurnina[b]

[a] *St. Petersburg State University, Universitetskii pr. 26, St. Petersburg, 198504 Russia*
[b] *Grebenshchikov Institute of Silicate Chemistry, Russian Academy of Sciences, St. Petersburg, Russia*

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Abstract — High-temperature mass spectrometry was used to determine the Gibbs energies, activities, and chemical potentials of SrO and SiO_2 in glasses and melts of the $SrO–SiO_2$ system in the temperature range 1840–1970 K. Negative deviations from the ideal behavior were revealed in the system. The standard enthalpies of formation and atomization of gaseous $SrSiO_2$ and $SrSiO_3$ were determined.
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The information on vaporization and thermodynamic properties of glasses and melts of the $SrO–SiO_2$ system is important for modeling physicochemical properties of multicomponent silicate glasses containing strontium oxide, aiming at preparing materials with preset properties. Among such materials are special-purpose multicomponent liquating glasses [2, 3], boron- and lead-free glazes [3, 4], and borosilicate glasses for radioactive waste disposal [5–7].

Phase equilibria in the $SrO–SiO_2$ system are fairly well understood [8] and presented in Fig. 1. Glasses in the given system are formed in the range 1.4–19.9 mol% SrO [2].

The aim of the present work was to study the composition of vapor over glasses and melts of the $SrO–SiO_2$ system, as well as the thermodynamic properties of the components of this system by means of high-temperature mass spectrometry.

Vaporization of SrO. When heated in neutral conditions, SrO vaporizes with almost complete dissociation into atomic strontium and oxygen, and a small part of SrO sublimes without decomposition [9].

Strontium oxide was obtained by fairly long heating of strontium carbonate in a vacuum at ~1400 K. Therewith, vacuum worsened due to dissociation of the salt and evolution of CO_2. As the sample was further heated in a molybdenum chamber (weakly reducing conditions) at 1983 K, in the mass spectra of the vapor we observed Sr^+, SrO^+, $SrMoO_4^+$, $SrMoO_3^+$, MoO_3^+, and MoO_2^+ ions in a 1 : 0.01 : 0.062 : 0.013 : 0.005 : 0.012 ratio. The origin of these ions in the mass spectra of the vapor over SrO has been considered in detail in [10]. To deduce equations for the dependence of the partial pressures of SrO and Sr over individual strontium oxide on temperature, we plotted the ion currents of SrO^+ and Sr^+ in the mass spectra of the vapor over SrO against reciprocal temperature in the range 1744–1983 K and measured the partial pressures of strontium oxide and atomic strontium by the method of comparison of ion currents, using gold as pressure standard [11]. The temperature dependences of the partial pressures of SrO and Sr (Pa) can be described by Eqs. (1) and (2), respectively.

$$\log p(\mathrm{SrO}) = -(28121 \pm 830)/T + (12.48 \pm 0.17), \quad (1)$$

$$\log p(\mathrm{Sr}) = -(2195 \pm 654)/T + (11.6 \pm 0.08). \quad (2)$$

Vaporization of SiO_2. Vaporization of individual silicon dioxide has been studied in sufficient detail [12]. In the range 1807–1976, the partial pressure of silicon monoxide is described by Eq. (3).

$$\log p(\mathrm{SiO,\ Pa}) = -(24676 \pm 552)/™ + (13.07 \pm 0.01). \quad (3)$$

Vaporization and thermodynamic properties of the components of the $SrO–SiO_2$ system. As seen from the phase diagram of the $SrO–SiO_2$ system [8] (Fig. 1), in the range 1840–1970 K, there are both heterogeneous regions and a homogeneous melt region, and the condensed phase contains three com-

[1] For communication I, see [1].

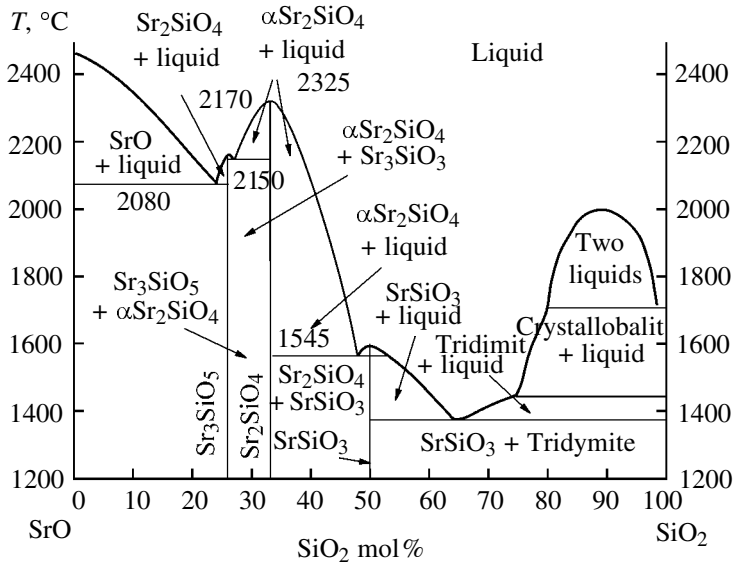

Fig. 1. Phase diagram of the $SrO–SiO_2$ system [8].

pounds: $SrO \cdot SiO_2$ (1 : 1), $2SrO \cdot SiO_2$ (2 : 1), and $3SrO \cdot SiO_2$ (3 : 1).

We studied the composition of the vapor over the $SrO–SiO_2$ system in the composition range 10–90 mol % SrO and determined the activities of its components. The mass spectra of the vapor over samples with varied contents of the $SrO–SiO_2$ system components in the range 1840–1970 K contained SiO^+, Sr^+, SrO^+, MoO_2^+, MoO_3^+, $SrMoO_4^+$, and $SrMoO_3^+$ ions. The intensity ratio of these ion currents depended both on the temperature and on the composition of the condensed phase of the system. To determine the molecular composition of the vapor over the samples, we measured the appearance energies of ions in the vapor mass spectra by the method of vanishing current, using gold as standard [11]. The appearance energy of $SrMoO_3^+$ was not measured because of the low intensity of this ion current. The SiO^+, SrO^+, Sr^+, MoO_2^+, MoO_3^+, and $SrMoO_4^+$ ions are molecular, because the ionization efficiency curves have no inflections, and the appearance energies coincide, within error, with the ionization energies of the corresponding molecules [10, 13].

The mass spectra of the vapor over glasses and melts of the $SrO–SiO_2$ system, the dependences of ion currents on temperature and vaporization time, as well as the appearance energies of identified ions provide evidence to show that heating of the samples at 1840–1970 K results in vaporization of SiO, SrO, Sr, and oxygen. Reaction of the sample with the material of the chamber produces gaseous molybdenum oxides MoO_2 and MoO_3, as well as strontium molybdates $SrMoO_3$ and $SrMoO_4$ [10].

The activities of SrO and SiO_2 in glasses and melts of the $SrO–SiO_2$ system were determined by means of differential mass spectrometry, using Eqs. (4) and (5), respectively.

$$a_{SrO} = p_{SrO}/p^0_{SrO} = I_{SrO^+}/I^0_{SrO^+}, \quad (4)$$

$$a_{SiO_2} = p_{SiO_2}/p^0_{SiO_2} = (p_{SiO} \cdot p_O)/(p^0_{SiO} \cdot p^0_O) = (I_{SiO^+} \cdot I_{O^+})/(I^0_{SiO^+} \cdot I^0_{O^+}). \quad (5)$$

Here p_i, I_i, p_i^0, and I_i^0 are the partial pressures of molecular forms and the intensities of ion currents in the mass spectra of the vapor over the sample and individual oxides SrO or SiO_2, respectively. For standards in the determination of component activities we used individual strontium oxide and silicon dioxide placed in the reference chamber. Dissociation of silicon dioxide into gaseous monoxide and oxygen and reaction of samples with chamber material are similar to those described in [1, 10, 12]. The O^+ or O_2^+ ion current intensities proportional to the partial pressures of atomic and molecular oxygen in the vapor over the samples and standard were not measured because of the high background near *m/z* 16 and 32. In view of the fact that the partial pressures of molybdenum oxides and atomic oxygen are related to each other by Eq. (6), the partial pressure of atomic oxygen in Eq. (6) was replaced by Eq. (7), using Eq. (8).

$$MoO_3(gas) = MoO_2(gas) + O(gas), \quad (6)$$

Table 1. Intensities of SiO^+, SrO^+, MoO_3^+, and MoO_2^+ ion currents in the mass spectra of the vapor over the SrO–SiO_2 system and SrO and SiO_2 standards, and the activities of SrO and SiO_2, determined by Eqs. (7), (10), (4), and (9), at 1840, 1920, and 1970 K

x_{SrO}, wt %	T, K	I, over sample				I, over standards SiO_2 and SrO				a_{SiO_2}		a_{SrO}	
		SiO^+	MoO_3^+	MoO_2^+	SrO^+	SiO^+	MoO_3^+	MoO_2^+	SrO^+	(7)	(10)	(4)	(9)
10.0	1840	205	29	17.5	–	200	27	16	–	1.0	–	–	–
	1920	720	126	85.5	–	705	123	81	–	0.99	–	–	–
	1970	1534	241.8	195	0.6	1517	252	201	11.8	1.0	–	5.1×10^{-2}	–
20.0	1840	185	42	25	–	200	45	27	–	0.93	–	–	–
	1920	575	138	84	0.4	590	156	90	9.5	0.92	–	4.2×10^{-2}	–
	1970	1742	360	240	1.5	1800	372	255	23.4	1.0	0.75	6.4×10^{-2}	1.6×10^{-2}
30.0	1840	200	16.2	11.1	0.2	217.5	40.2	25.5	3.9	0.85	–	5.1×10^{-2}	–
	1920	628	44.5	39	0.6	723	51.8	34.5	10.7	0.66	–	5.6×10^{-2}	–
	1970	707	39	48	2.1	994	82.8	75.9	25.0	0.53	0.55	8.4×10^{-2}	4.0×10^{-2}
40.0	1840	325	14	11.5	0.2	345	16.7	10.4	3.6	0.71	–	5.6×10^{-2}	–
	1920	1125	51	43.5	0.7	1641	96.6	72.5	8.9	0.60	–	7.8×10^{-2}	–
	1970	2615	102	105	2.4	4539	224	193	26.2	0.48	0.38	9.2×10^{-2}	7.9×10^{-2}
50.0	1840	123	2.2	2.7	0.3	342	18.4	11.5	3.9	0.18	–	4.0×10^{-2}	–
	1920	335	8.2	10.5	0.5	1194	83	59	8.7	0.22	–	5.7×10^{-2}	–
	1970	651	21	27	1.6	2573	162	129	20.5	0.16	0.22	7.8×10^{-2}	0.16
60.0	1840	60	1.1	1.5	0.3	932	18.4	12.6	3.2	3.2×10^{-2}	–	9.4×10^{-2}	–
	1920	150	3.5	5.0	0.8	914	69	44.8	9.7	7.5×10^{-2}	–	8.2×10^{-2}	–
	1970	310	9.6	13.2	2.4	2301	218.5	172.5	22.7	7.7×10^{-2}	9.7×10^{-2}	0.10	0.30
66.7	1840	1.2	1.3	1.8	0.4	560	51	39	2.6	1.2×10^{-3}	–	0.15	–
	1920	8.5	0.5	1.6	0.7	1371	150	99	5.4	1.3×10^{-3}	–	0.13	–
	1970	25.5	0.9	3.9	1.8	2705	260	230	17.0	1.9×10^{-3}	3.9×10^{-2}	0.11	0.53
75.0	1840	–	–	–	2.3	–	–	–	2.3	–	–	1.0	–
	1920	1.8	0.3	0.9	5.8	1630	180	120	5.8	2.4×10^{-4}	–	1.0	–
	1970	4.8	0.8	2.8	18.3	3514	390	290	18.3	2.9×10^{-4}	–	1.0	–
80.0	1840	–	–	–	2.5	–	–	–	2.5	–	–	1.0	–
	1920	0.7	0.4	0.8	6.0	1560	146	98	6.0	1.6×10^{-4}	–	1.0	–
	1970	2.5	0.9	2.7	19.0	3398	365	268	19.0	1.8×10^{-4}	–	1.0	–
90.0	1840	–	–	–	2.4	–	–	–	2.4	–	–	1.0	–
	1920	–	–	–	5.7	–	–	–	5.7	–	–	1.0	–
	1970	2.1	0.6	2.5	18.6	3720	420	310	18.6	1.0×10^{-4}	–	1.0	–

$$a_{SiO_2} = I_{SiO^+}/I^0_{SiO^+}\left[\frac{I_{MoO_2^+}/I_{MO_3^+}}{I^0_{MoO_2^+}/I^0_{MO_3^+}}\right], \quad (7)$$

$$p_0 = K_e p_{MoO_2}/p_{MOO_3}. \quad (8)$$

Here K_e is the equilibrium constant of reaction (6).

In further research the activities of SiO_2 in glasses and melts of the SrO–SiO_2 systems were determined by measuring the intensities of the SiO^+, MoO_2^+, and MoO_3^+ ion currents in the mass spectra of the vapor over samples and individual silicon dioxide.

In the melts of the SrO–SiO_2 systems containing from 20 to 66.7 mol % of SrO, the activities of SrO and SiO_2 at 1970 K were additionally calculated by the Belton–Fruechan (9) [14] and Gibbs–Duhem equations (10), respectively.

$$\ln\gamma_{SrO}(x_{SrO}) = \int_{x_{SrO}=1}^{x_{SrO}=x_{SrO}} x_{SiO_2} d\left[\ln\frac{I^+_{SiO}}{I^+_{Sr}} - \ln\frac{x_{SiO_2}}{x_{SrO}}\right], \quad (9)$$

$$\ln\gamma_{SiO_2} = -\int_{\ln\gamma^0_{SrO}}^{\ln\gamma_{SrO}} (x_{SrO}/x_{SiO_2}) d\ln\gamma_{SrO}. \quad (10)$$

The activities of SrO and SiO_2 in glasses and melts of the SrO–SiO_2 system, obtained at 1840, 1920, and 1970 K, are listed in Table 1, and the plots of the components activities against the concentration of SrO at 1920 and 1970 K are presented in Fig. 2. In the

samples with low SrO or SiO_2 contents, the component activities were determined only at those temperatures at which the SiO^+, MoO_3^+, MoO_2^+, and SrO^+ ion current intensities were higher than the sensitivity of the mass spectrometer.

The component activities of the melt of the SrO–SiO_2 system, determined at 1970 K by the method of comparison of ion currents and by Belron–Fruechan fairly fit each other.

To determine the component activities of melts by Eqs. (9) and (10), one should extrapolate the $x(SiO_2) = f[\ln(I^+_{SiO}/I^+_{Sr}) - \ln(x_{SiO_2}/x_{SrO})]$ and $x_{SrO}/x_{SiO_2} = f\ln\gamma_{SiO_2}$ plots to zero –(SiO_2) and x_{SrO}/x_{SiO_2} values, respectively, which brings additional errors in the resulting values. The errors in the activities determined by the method of comparison of ion currents are ~5–10% for SrO and 8–15% for SiO_2. Since the activities of SrO and SiO_2, determined by Eqs. (9) and (10), were calculated for a narrow concentration range, the thermodynamic properties of the SrO–SiO_2 system were considered using values calculated by Eqs. (4) and (7).

The chemical potentials ($\Delta\mu_i$), excess chemical potentials ($\Delta\mu_i^{\partial}$), Gibbs energies (ΔG), and excess Gibbs energies (ΔG^{∂}) of the components in glasses and melts of the SrO–SiO_2 system were calculated by Eqs. (11)–(14).

$$\Delta G = \Sigma x_i \Delta\mu_i, \quad (11)$$

$$\Delta\mu_i = RT\ln a_i, \quad (12)$$

$$\Delta G^{\partial} = \Sigma x_i \Delta\mu_i^E, \quad (13)$$

$$\Delta\mu_i^E = RT\ln\gamma_i. \quad (14)$$

The resulting values are listed in Table 2, and the plots of $\Delta\mu_i$, $\Delta\mu_i^{\partial}$, ΔG, and ΔG^{∂} against the composition of the condensed phase of the SrO–SiO_2 system are shown in Figs. 3 and 4.

The activities of SrO and SiO_2, determined in the present work, are in a good agreement with the phase diagram of the system [8]. In the melt region, a negative deviation from ideality is observed, implying that the system components actively interact with each other to form new chemical bonds and, a result, new chemical compounds. The formation of the silicate melt from strontium oxide and silicon dioxide involves strong chemical interaction with cleavage of two bridging Si–O–Si bonds and formation on their place of two terminal oxygen atoms. The plots of ΔG and ΔG^{∂} on the composition of the condensed phase show a minimum at the strontium silicate composition, whose presence derives from the fact that all bridging atoms and free oxygens convert into nonbridging [15].

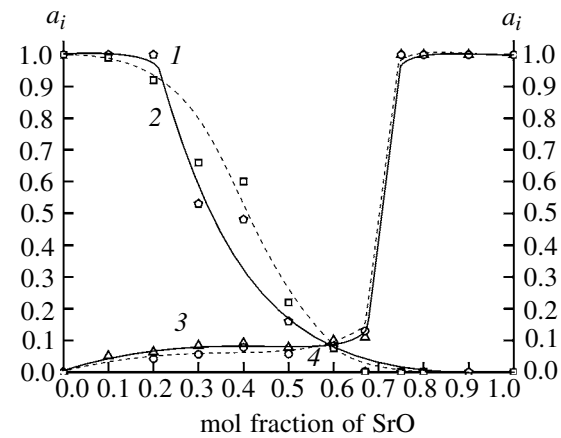

Fig. 2. Plot of component activities (a_i) vs. SrO concentration in the condensed phase of the SrO–SiO_2 system at 1920 and 1970 K. (*1*) SiO_2, 1970 K; (*2*) SiO_2, 1920 K; (*3*) SrO, 1970 K; and (*4*) SrO, 1920 K.

The position of these minimum agrees well with the results in [16], obtained in determining the enthalpy of formation of in the SrO–SiO_2 system from 1 mol of the oxides at 298 K.

When comparing the thermodynamic parameters determined in glasses and melts of the SrO–SiO_2 and BaO–SiO_2 systems [1], one can note that the degree of the negative deviation of the melts of these two systems from the ideal behavior depends on the acid–base properties of the modifier oxide. Comparison of the Gibbs energies of mixing in the SrO–SiO_2 and BaO–SiO_2 systems shows that the deviation depends on the type of the modifier cation and the polymerization degree of silicate anions and becomes more negative in going from the first system to the second.

Since the vapors over the barium silicate [1, 17] and calcium silicate systems [18] were shown to contain gaseous silicates, whereas that over the SrO–B_2O_3–SiO_2 system, SrSiO molecules [19], we made an attempt to find strontium silicates in the vapor over the SrO–SiO_2 system, too. Vaporization was performed from a single tungsten chamber, since, as mentioned above, using a molybdenum chamber we found in the vapor over the strontium silicate system molybdenum oxides MoO_2 and MoO_3 and in the vapor mass spectrum, MoO_2^+ and MoO_3^+ ions at the same *m/z* values as the $SrSiO_2^+$ and $SrSiO_3^+$ ions, respectively.

In the mass spectra of the vapor over the starting composition (66.7 mol% SrO –33.3 mol% SiO_2) in the temperature range 2180–2340 K we detected Sr^+, SrO^+, SiO^+, SiO_2^+, WO_2^+, WO_3^+, $SrWO_4^+$, $SrWO_3^+$, $SrSiO^+$, $SrSiO_2^+$, and $SrSiO_3^+$ ions. Comparison of the

Table 2. Chemical and excess chemical potentials of SrO and SiO_2, and Gibbs energies and excess Gibbs energies in the SrO–SiO_2 system at 1840, 1920, and 1970 K, obtained in the present work

Content of SrO, mole fraction	T, K	$-\Delta\mu$, kJ mol^{-1}		$-\Delta\mu_i^E$, kJ mol^{-1}		$-\Delta G$, kJ	$-\Delta G^E$, kJ
		SrO	SiO_2	SrO	SiO_2		
0.10	1840	–	0	–	–1.61	–	–
	1920	–	0.16	–	–1.52	–	–
	1970	48.70	0	11.03	–1.73	4.87	0.45
0.20	1840		1.11		–2.30		
	1920	50.60	1.33	24.91	–2.23	11.19	3.20
	1970	45.00	0	18.66	–3.65	9.00	0.81
0.30	1840	45.53	2.49	27.11	–2.97	15.40	6.05
	1920	46.01	6.63	26.79	–0.94	18.45	8.70
	1970	40.60	10.40	20.85	–4.56	19.45	9.44
0.40	1840	44.09	5.24	30.08	–2.58	20.78	10.49
	1920	40.72	8.15	26.10	0	21.18	10.44
	1970	39.08	12.02	24.07	3.65	22.84	11.82
0.50	1840	49.24	26.23	38.64	15.63	37.74	27.13
	1920	45.73	24.17	34.66	13.11	34.95	23.88
	1970	41.78	30.02	30.43	–18.66	35.89	24.55
0.60	1840	36.17	52.66	28.36	38.64	42.76	32.47
	1920	39.92	41.35	31.77	26.72	40.49	29.75
	1970	37.71	41.99	29.35	26.98	39.43	28.40
0.67	1840	29.02	102.88	22.90	85.92	53.40	43.69
	1920	32.57	106.08	26.18	88.38	56.83	46.70
	1970	36.15	102.63	29.59	84.47	58.09	47.70
0.75	1840	0	–	–4.40	–	–	–
	1920	0	133.05	–4.59	110.92	33.26	24.29
	1970	0	133.41	–4.71	110.71	33.35	24.14
0.80	1840	0	–	–3.41	–	–	–
	1920	0	139.52	–3.56	113.83	27.90	19.92
	1970	0	141.23	–3.65	114.87	28.25	20.05
0.90	1840	0	–	–1.61	–	–	–
	1920	0	–	–1.69	–	–	–
	1970	0	150.85	–1.73	113.14	15.09	9.76

measured appearance energies of the ions with those reported in [1, 10, 13] showed that the vapor contains strontium, silicon, and tungsten oxides, atomic strontium, oxygen, as well as strontium tungstates and silicates. The partial pressures of the molecular forms of the vapor were determined by the method of comparison of ion currents with gold as pressure standard [11]. The ionization cross sections of the molecular forms were calculated by the additivity method with use of atomic cross sections [20].

To determine the standard enthalpies of formation of gaseous strontium silicates, we measured the equilibrium constants of gas-phase reactions (15) and (16) and calculates the enthalpies of these reactions by Eqs. (17) and (18).

$$SrO + SiO = SrSiO_2, \quad (15)$$

$$SrO + SiO_2 = SrSiO_3, \quad (16)$$

$$\Delta_r H^0(T) = -R\,\frac{\partial \ln K_e(T)}{\partial(1/T)}, \quad (17)$$

$$\Delta_r H^0(0) = T[\Delta_r \Phi^0(T) - R\ln K_e(T)]. \quad (18)$$

Here $\Delta_r H^0(0)$, $\Delta_r H^0(™)$, and $\Delta_r \Phi^0(™)$ are the changes of the reaction enthalpy and reduced Gibbs energy at the temperatures 0 and ™, respectively; R, gas constant; and K_e, equilibrium reaction constant.

To determine the standard enthalpy of formation of SrSiO(gas), we made an attempt to measure the equilibrium constants of gas-phase reactions (19) and (20).

$$2SrSiO_2 = SrSiO + SrSiO_3, \quad (19)$$

$$Sr + SiO = SrSiO. \quad (20)$$

The intensity of the $SrSiO^+$ ion current continuously decreased. The partial pressure of SrSiO did not react adequately to varied temperature and to either increased or decreased partial pressures of Sr, SiO, $SrSiO_2$, and $SrSiO_3$. For this reason, we failed to measure the enthalpies of reactions (19) and (20), and the mechanism of appearance of the SrSiO species remained unknown.

The thermodynamic functions of gaseous oxides, required for calculation of the enthalpies of reactions (15) and (16) were taken from [21], and those of $SrSiO_3$ and $SrSiO_2$(gas) were calculated by means of statistical thermodynamics in the «rigid rotator–harmonic oscillator» approximation. For the $SrSiO_2$ and $SrSiO_3$ molecules we accepted cyclic structures of C_{2v} symmetry, analogous to the molecular structures of barium silicates [1, 17]. The interatomic distances and normal mode frequencies for the SiO_2 and SiO_3 were taken equal to those in $BaSiO_2$ and $BaSiO_3$ [1, 17]: r(Si–O) 1.63 Å for both molecules, r(Si=O) 1.55 Å, and OSiO angle 101° for $SrSiO_3$ and 104° for $SrSiO_2$. The normal mode frequencies for $SrSiO_2$ were taken to be 922, 874, 478, 120, 75, and 65 cm^{-1} and for $SrSiO_3$, 1237, 924, 849, 490, 421, 411, 120, 75, and 65 cm^{-1}. The thermodynamic functions of gaseous $SrSiO_2$ and $SrSiO_3$ were calculated with Sr–O interatomic distances and normal mode frequencies equal to those in strontium tantalates and niobates [22, 23].

The enthalpies of reactions involving gaseous $SrSiO_2$ and $SrSiO_3$, calculated by Eqs. (17) and (18) and reduced to the standard temperature 298 K, were –366 ± 48 and –36 ± 5 for reaction (15) and –505 ± 56 and –505 ± 5 kJ mol^{-1} for reaction (16), respectively. By combining the weighted average enthalpies of reactions (15) and (16), reduced to 298 K, with the heats of formation of gaseous SrO, SiO, and SiO_2 [21] we could calculate the standard enthalpies and atomization of gaseous strontium silicates: –474 ± 18 and 1583 ± 20 for $SrSiO_2$; and –841 ± 20 and 2199 ± 22 kJ mol^{-1} for $SrSiO_3$.

The standard enthalpies of formation of gaseous strontium silicates are less negative than those of barium silicates [1], which is nicely consistent with the trends in the thermal stability of gaseous salts of oxygen-containing acids [24]. Our present data together with known enthalpies of atomization of gaseous strontium salts, systematized in [10, 24–30], allowed us to obtain, for the isocationic series of gaseous strontium salts, the dependence of the standard enthalpies of atomization of salts and the enthalpies of atomization of anion-forming oxides [24], represented by Eq. (21). The coefficients k and b of Eq. (21) were 1.028 ± 0.017 and 896.2 ± 26.8, respectively.

$$\Delta_{at}H^0(M_mXO_n, gas, 298) = k\Delta_{at}H^0(XO_{n-1}, gas, 298) + b. \quad (21)$$

The high regression coefficient (0.998) and the standard deviation of 70.3 provide evidence for the validity of our obtained standard enthalpies of formation and atomization of gaseous $SrSiO_2$ and $SrSiO_3$.

EXPERIMENTAL

The work was performed by high-temperature mass spectrometry on an MS-1301 mass spectrometer at an ionizing energy of 25 V. The block of double molybdenum one-temperature effusion chambers was heated by electronic bombardment. The temperature was measured with an EOP-66 optical pyrometer with an accuracy of ±5° in the range 1600–2300 K. The instrument was preliminarily calibrated by CaF_2 vapor pressure [21, 31].

The SrO–SiO_2 system was synthesized using strontium carbonate of special purity grade and silicon dioxide of pure grade as starting materials. Glasses and ceramic samples of the system were synthesized in a platinum crucible in a silit oven at 1473–2063 K for 2 h. The load was ground in an agate mortar for 2 h. Ceramic samples were calcined in two stages in platinum crucibles in air in a silit oven at temperatures lower the solidus point. The quality of the synthesized samples was controlled by X-ray phase and chemical analyses.

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REFERENCES

1. Tyurnina, Z.G., Stolyarova, V., Shugurov, S.M., and Lopatin, S.I., *Zh. Obshch. Khim.,* 2006, vol. 76, no. 10, p. 1588.
2. Milyukov, E.M. and Kasymova, S.S., *Nesmeshivayuschiesya rasplavy i stekla* (Immiscible Melts and Glasses), Tashkent: FAN, 1981.
3. Appen, A.A., *Khimiya stekla* (Chemistry of Glass), Leningrad: Khimiya, 1974.

4. Shteinberg, Yu.G., *Strontsievye glazuri* (Strontium Glazes), Moscow: Stroiizdat, 1967.
5. Sobolev, I.A., Ozhovan, M.I., Shcherbatova, T.D., and Batyukhina, O.G., *Stekla dlya radioaktivnykh otkhodov* (Glasses for Radioactive Wastes), Moscow: Energoatomizdat, 1999.
6. Ojovan, M.I. and Lee, W.E., *An Introduction to Nuclear Waste Immobilisation,* Sheffield: Elsevier, 2005.
7. Lyashenko, A.V., *SVCh-immobilizatsiya vysokoaktivnykh promyshlennykh otkhodov* (Miscowave Immobilization of Highly Radioactive Industrial Wastes), Moscow: Nauka, 2004.
8. *Diagrammy sostoyaniya silikatnyh system* (Phase Diagrams of Silicate Systems), Toropov, N.A. and Barzakovskii, L., Eds., Leningrad: Nauka, 1969, vol. 1.
9. Kazenas, E.K. and Tsvetkov, Yu.V., *Isparenie oksidov* (Vaporization of Oxides), Moscow: Nauka, 1997.
10. Lopatin, S.I., Semenov, G.A., and Shugurov, S.M., *Zh. Obshch. Khim.,* 2003, vol. 73, no. 2, p. 187.
11. Paule, R.C. and Mandel, J., *Pure Appl. Chem.,* 1972, vol. 31, no. 3, p. 397.
12. Bondar', V.V., Lopatin, S.I., and Stolyarova, V.L., *Neorg. Mater.,* 2005, vol. 41, no. 4, p. 434.
13. *Energii razryva khimicheskih svyazei. Potentsialy ionizatsii i srodstvo k elektronu* (Dissociation Energies of Chemical Bonds. Ionization Potentials and Electron Affinities), Kondrat'ev, V.N., Ed., Moscow: Nauka, 1974.
14. Belton, G.R. and Fruechan, R.J., *Mettallurg. Trans.,* 1970, vol. 1, no. 4, p. 781.
15. Anfilogov, V.N., Bykov, V.N., and Osipov, A.A., *Silikatnye rasplavy* (Silicate Melts), Moscow: Nauka, 2005.
16. Hess, P.C., *Rev. Miner.,* 1995, vol. 32, p. 145.
17. Cordfunke, E.H.P., Groen, C.P., Huntelaar, M.E., Alexander, C.A., and Ogden, J.S., *J. Chem. Thermodyn.,* 2000, vol. 32, no. 3, p. 839.
18. Stolyarova, V.L., Shornikov, S.I., Ivanov, G.G., and Shultz, M.M., *J. Electrochem. Soc.,* 1991, vol. 138, no. 12, p. 3710.
19. Asano, M. and Kou, T., *J. Chem. Thermodyn.,* 1990, vol. 22, no. 12, p. 1223.
20. Mann, J.B., *J. Chem. Phys.,* 1967, vol. 46, no. 5, p. 1646.
21. *Termodinamicheskie svoistva individual'nyh veschestv* (Thermodynamic Properties of Individual Substances), Glushko, V.P., Ed., Moscow: Akad. Nauk SSSR, 1978–1984, vols. 1–4.
22. Lopatin, S.I., Semenov, G.A., and Pilyugina, T.S., *Zh. Obshch. Khim.,* 1999, vol. 69, no. 11, p. 1761.
23. Semenov, G.A. and Lopatin, S.I., *Zh. Obshch. Khim.,* 2001, vol. 71, no. 6, p. 884.
24. Lopatin, S.I., *Doctoral (Chem.) Dissertation,* St. Petersburg, 2001.
25. Lopatin, S.I., Shugurov, S.M., and Semenov, G.A., *Dokl. Ross. Akad. Nauk,* 2002, vol. 386, no. 5, p. 649.
26. Lopatin, S.I., Shugurov, S.M., and Semenov, G.A., *Rapid Commun. Mass Spectrom.,* 2004, vol. 18, no. 1, p. 112.
27. Lopatin, S.I., Shugurov, S.M., and Semenov, G.A., *Zh. Obshch. Khim.,* 2003, vol. 73, no. 12, p. 1972.
28. Shugurov, S.M. and Lopatin, S.I., *J. Chem. Thermodyn.,* 2005, vol. 37, no. 7, p. 721.
29. Shugurov, S.M., Lopatin, S.I., Semenov, G.A., and Stolyarova, V.L., *Zh. Obshch. Khim.,* 2005, vol. 75, no. 3, p. 357.
30. Shugurov, S.M., Lopatin, S.I., Semenov, G.A., and Stolyarova, V.L., *Zh. Obshch. Khim.,* 2005, vol. 75, no. 8, p. 1252.
31. Zaitsev, A.I., Korolev, N.V., and Mogutnov, B.M., *Teplofiz. Vys. Temp.,* 1989, vol. 27, no. 3, p. 465.