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Thermodynamic Properties of Silicate Glasses and Melts: IX.[1] Bi_2O_3–SiO_2 System

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Abstract—Differential high-temperature mass spectrometry was used to determine the activities of Bi_2O_3 in Bi_2O_3–SiO_2 glasses at 1000 K. The activities of SiO_2 and integral Gibbs energies in Bi_2O_3–SiO_2 glasses were determined. Negative deviations from the ideal behavior were revealed in the studied system at 1000 K.

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Materials on the basis of a Bi_2O_3–SiO_2 system are widely used in practice [2]. The information on the vaporization and thermodynamic properties of the components of this system is necessary for high-temperature synthesis, modeling of physicochemical properties, and service of such materials. The latter includes low-melting solder glasses for electronics, glass ceramics for optical and electronic devices, thermal and mechanical sensors for analytical control, laser and luminescent materials, as well as fiber optic guides for new-generation communication means.

Phase equilibria for stable and metastable states of the Bi_2O_3–SiO_2 system have been studied in numerous works [3–8]. The glass-forming ranges in this system are listed in the reference book [9]. Scarce information is available in the literature on the vaporization of Bi_2O_3–SiO_2 glasses and melts. High-temperature heat capacities and activities at 1373 K were determined for Bi_2O_3 from, respectively, the phase diagrams of stable and metastable equilibria were determined in [10, 11].

The individual oxides in the Bi_2O_3–SiO_2 system have quite different volatilities [12]. When heated in neutral conditions to 1000–1200 K, bismuth(III) oxide vaporizes primarily as atomic bismuth (Bi_2) and molecular oxygen [13–16]. The vapor over Bi_2O_3 also contains Bi_4O_6, Bi_4O_5, Bi_4O_4, Bi_3O_4, Bi_2O_3, Bi_2O_2, Bi_2O, and BiO. The total pressure of these oxides at 1000 K comprises no more than 1–2% of the partial pressure of atomic bismuth. Silicon dioxide vaporizes at 1800–2050 K with dissociation into gaseous silicon monoxide and oxygen. The equations of the temperature dependences of the vapor pressure of molecular forms of Bi over Bi_2O_3 and of SiO over SiO_2 are reported in [13] and [17], respectively.

Minaeva et al. [18] studied the vaporization and thermodynamic functions of mixing of Bi_2O_3–B_2O_3 glasses and melts in the temperature range 1120–1310 K. Melts of the Bi_2O_3–B_2O_3 system show negative deviations from ideality, which are associated with reactions between the components in the condensed and gas phases, whereas in the concentration range 10–30 mol % Bi_2O_3, an immiscibility region for B_2O_3 takes place. Nikolaev et al. [19] studied the vaporization of the components of the glass-forming system Bi_2O_3–GeO_2 and determined the partial pressures of the main molecular forms in vapor over glasses and melts of this system in the temperature range 1260–1520 K. The gas phase over bismuth phosphates in the temperature range 1400–1550 K was found to contain the complex associates $BiPO_3$, BiP_2O_6, and BiP_3O_9 [20]. As shown in [21, 22], alkali metal bismuthates vaporize congruently without dissociation.

In the present work we studied, for the first time, vaporization processes and glass temperature mixing thermodynamics in the Bi_2O_3–SiO_2 system at 1000 K by high-temperature mass spectrometry. In the mass spectra of the vapor over an individual bismuth oxide Bi_2O_3 and Bi_2O_3–SiO_2 glasses in the temperature range 950–1050 K, we identified Bi^+ ions (appearance

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

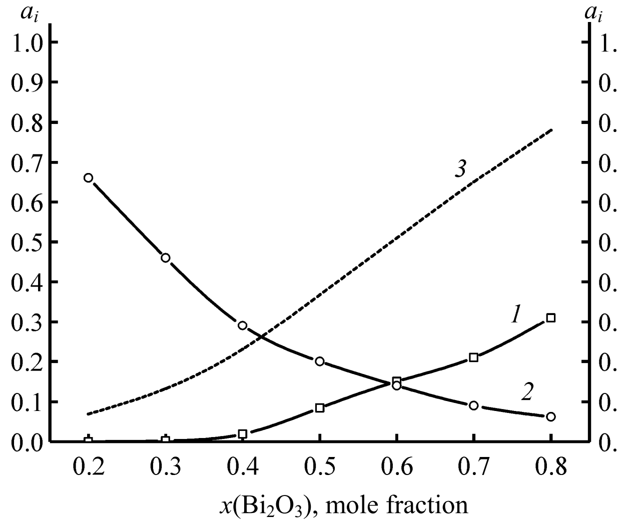

Fig. 1. Plots of the activities of (*1*) Bi_2O_3 ($a_i \times 10$) and (*2*) SiO_2 in the Bi_2O_3–SiO_2 system, obtained in the present work, against the mole fraction of Bi_2O_3 at 1000 K (*3*) activities of Bi_2O_3 at 1373 K, calculated in [10].

energy 7.4±0.3 eV). The mass spectra of the vapor at a higher temperature (1200 K) contained Bi^+, Bi_2^+, BiO^+, and $Bi_4O_6^+$ ions. As the temperature was raised, the Bi^+, Bi_2^+, BiO^+, and $Bi_4O_6^+$ ion currents gradually decreased because of a change in the composition of the condensed phase, specifically, its enrichment with SiO_2 due to selective vaporization of Bi_2O_3. Silicon monoxide ions appeared in the mass spectra at temperatures above 1800 K, when bismuth-containing ions were no longer observed.

The Bi^+ ions are molecular ions, as evidenced by the fact that the ionization efficiency curves contain no bends, which the appearance energy of Bi^+ coincides, within error, with the ionization energy of atomic bismuth [23]. The vaporization process of bismuth oxide at 950–1050 K is described by reaction (1).

$$Bi_2O_3\ (l) = 2Bi\ (gas) + 1.5O_2\ (gas). \quad (1)$$

The activity of Bi_2O_3 was determined by means of differential mass spectrometry using individual Bi_2O_3 as standard [Eq. (2)]:

$$A(Bi_2O_3) = \frac{p(Bi_2O_3)}{p_0(Bi_2O_3)} = \frac{p^2(Bi)p^{1.5}(O_2)}{p_0^2(Bi)p_0^{1.5}(O_2)}. \quad (2)$$

The partial pressure of molecular oxygen in Eq. (2) was calculated by Eq. (3).

$$p(O_2) = 0.75p(Bi)\sqrt{M(O_2)/M(Bi)}. \quad (3)$$

Here a_i is the activity of the *i*th component; p_i, molecular partial pressure of the *i*th vapor component, and *M*, molecular weight of the *i*th vapor component.

Based on the hypothesis of freezing-out of structure fluctuations of melts during their glass transition [24, 25], we assumed that the thermodynamic approaches to assessing the properties of melts can be used to assess the thermodynamic properties of glasses.

The activities of silicon oxide in the Bi_2O_3–SiO_2 system were obtained by the Gibbs–Duhem equation (4).

$$\log\frac{a(SiO_2)}{x(SiO_2)} = -\int_{x(Bi_2O_3)=0}^{x(Bi_2O_3)=x(Bi_2O_3)} \frac{x(Bi_2O_3)}{x(SiO_2)}\, d\log\frac{a(Bi_2O_3)}{x(SiO_2)}. \quad (4)$$

Here x_i is the concentration of the *i*th oxide in Bi_2O_3–SiO_2 glasses.

The activities of the components of Bi_2O_3–SiO_2 glasses at 1000 K are presented in the table and Fig. 1. The chemical potentials ($\Delta\mu_i$), excess chemical potentials ($\Delta\mu_i^E$), Gibbs energies of formation from the oxides (ΔG), and excess Gibbs energies (ΔG^E) in Bi_2O_3–SiO_2 glasses were calculated by Eqs. (5)–(8) and presented in the table and Eqs. (2) and (3).

$$\Delta\mu_i = RT\ln a_i, \quad (5)$$

$$\Delta\mu_i^E = RT\ln (a_i/x_i), \quad (6)$$

$$\Delta G = \sum_i x_i\Delta\mu_i, \quad (7)$$

$$\Delta G^E = \sum_i x_i\Delta\mu_i^E. \quad (8)$$

In Fig. 1 we compare the activities of Bi_2O_3, obtained in the present work in Bi_2O_3–SiO_2 glasses at 1000 K and calculated in [1] from data on phase equilibria at 1373 K. Negative deviations from ideality are observed for the Bi_2O_3–SiO_2 system both in the first and second case. However, the different degrees of deviation from the ideal behavior of the system in study are likely to be associated with much different experimental temperatures. The negative deviations from ideality are probably explained by the fact that the glasses contain, according to the phase diagram of the Bi_2O_3–SiO_2 system, thermodynamically stable compounds $Bi_4Si_3O_{12}$ and $Bi_{12}SiO_{20}$ [3–8]. Evidence for this assumption comes from the calculations of the fractions of different structural chemical units in glasses and glass-forming melts, in particular, in terms of the theory of ideal associated solutions, for glasses and melts of the Na_2O–B_2O_3 [26], Na_2O–SiO_2 [27], Rb_2O–B_2O_3 [28], and Cs_2O–B_2O_3 systems [29].

Thermodynamic functions of mixing for the Bi_2O_3−SiO_2 system at 1000 K, obtained in the present work (component activities, chemical potentials, and Gibbs formation energies and corresponding excess values)

Fraction of oxides in glasses, mol %		a_i		$-\Delta\mu_i$, kJ/mol		$-\Delta\mu_i^E$, kJ/mol		$-\Delta G$, kJ/mol	$-\Delta G^E$, kJ/mol
Bi_2O_3	SiO_2	Bi_2O_3	SiO_2	Bi_2O_3	SiO_2	Bi_2O_3	SiO_2		
20	80	1.95×10^{-5}	0.66	90.2	3.5	76.8	1.6	20.8	16.7
30	70	2.07×10^{-4}	0.46	70.5	6.4	60.5	3.4	25.6	19.6
40	60	1.93×10^{-3}	0.29	52.0	10.2	44.3	5.9	26.9	21.3
50	50	8.4×10^{-3}	0.20	39.7	13.6	34.0	7.8	27.7	22.3
60	40	1.5×10^{-2}	0.14	34.9	16.3	30.7	8.7	27.5	22.9
70	30	2.1×10^{-2}	0.09	32.1	19.2	29.2	9.2	28.2	23.2
80	20	3.1×10^{-2}	6.2×10^{-2}	28.9	23.1	27.0	9.7	28.4	23.6

The change of the Gibbs formation energy and the corresponding excess value in Bi_2O_3–SiO_2 glasses at 1000 K compares, in order of magnitude, values relating to the thermodynamic behavior of the binary systems Bi_2O_3–B_2O_3 [18], GeO_2–SiO_2 [30–32], and GeO_2–B_2O_3 [31–33], but much differ from the respective values (by a factor of 4–5) for alkaline borate and alkaline silicate systems [26–29, 31, 32]. As shown in numerous studies [31, 32, 34–36], the observed changes in the thermodynamic properties of binary oxide glasses and melts can be explained in terms of the acid–base concept [37], using one of the criteria of this concept for isothermal conditions, specifically, the difference in electronegativity between the oxides forming a binary system. The acid–base concept as a tool to gain insight into vaporization of components of oxide systems [38] was further developed in [32, 34–36] to account for factors controlling the possibility of associate formation in the gas phase over oxide systems, in particular, the volatility ratio of individual oxides forming an oxide system in isothermal conditions. Just this factor appears to explain why bismuth silicates are lacking from the vapor over Bi_2O_3–SiO_2 glasses in spite of a

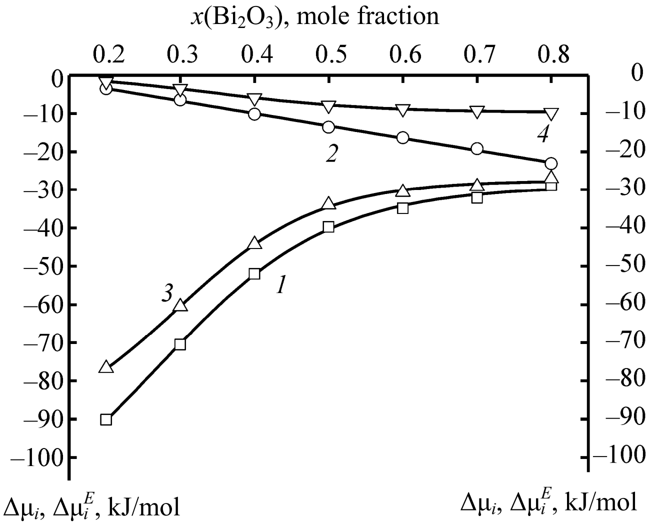

Fig. 2. Plots of the chemical potentials ($\Delta\mu$) and excess chemical potentials ($\Delta\mu^E$) of (*1*, *3*) Bi_2O_3 and (*2*, *4*) SiO_2 in the Bi_2O_3−SiO_2 system against the mole fraction of Bi_2O_3 at 1000 K.

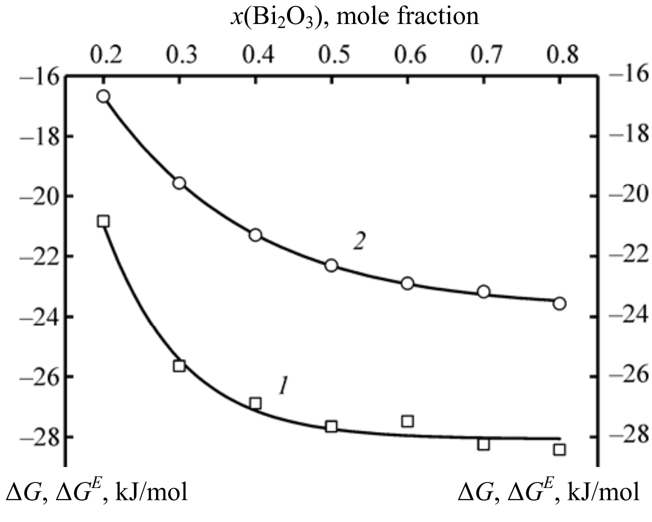

Fig. 3. Plots of the (*1*) Gibbs energies (ΔG) and (*2*) excess Gibbs energies in the Bi_2O_3−SiO_2 system against the mole fraction of Bi_2O_3 at 1000 K.

considerable difference in the electronegativities of Bi_2O_3 and SiO_2 [35]. The same regularity was established in [30] for the GeO_2–SiO_2 system.

EXPERIMENTAL

The work was performed by high-temperature mass spectrometry on an MS-1301 instrument at an ionizing energy of 25 eV. The samples were vaporized from a twin molybdenum effusion cell with the inner surface coated with an iridium thin film. The cell with samples was heated with a resistance furnace, the temperature was measured with a platinum/platinum–rhodium thermocouple with an accuracy of ±1 K in the temperature range 900–1400 K. The instrument was preliminarily calibrated by CsCl vapor pressure [39]. The samples of the Bi_2O_3–SiO_2 system were prepared from spectral grade oxides. The Bi_2O_3–SiO_2 glasses were synthesized in Al_2O_3 crucibles at 1273–1823 K. The synthesis tem-perature and time were determined by the evolution of volatile bismuth oxide. The Bi_2O_3–SiO_2 glass-forming range obtained in the present work corresponds to that in [40].

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