Thermodynamic properties of the liquid Bi₂O₃-SiO₂ solutions were determined from the results of the electrochemical measurements by use of the solid oxide galvanic cells with YSZ (Yttria-Stabilized-Zirconia) electrolyte. Activities of Bi₂O₃ in the solutions were determined for 0.2, 0.3, 0.4, and 0.5 SiO₂ mole fractions in the temperature range 1073-1293 K from measured electromotive force (e.m.f) of the solid electrolyte galvanic cell:

\[ \text{Bi, Bi}_2\text{O}_3\cdot\text{SiO}_2 | \text{YSZ} | \text{air (p}_\text{O}_2 = 0.213 \text{ bar)} \]

Additionally, heat capacity data obtained for two solid phases 6Bi₂O₃·SiO₂ and 2Bi₂O₃·3SiO₂ were included into optimization of thermodynamic properties of the system. Optimization procedure was supported by differential thermal analysis (DTA) data obtained in this work as well as those accepted from the literature.

Using the data obtained in this work, and the information about phase equilibria found in the literature, binary system Bi₂O₃-SiO₂ was assessed with the ThermoCalc software.

Key words: Bismuth silicate; Galvanic cell; Phase diagram; Thermodynamics; Activity

1. Introduction

The thermodynamic properties of liquid solutions occurring in Kaldo process [1], namely, metallic phase and the slag phase must be known for the prediction of behaviour of impurity distribution under fixed temperature and the partial oxygen pressure. The metal phase consists of silver as a solvent with the most common solutes which are the bismuth, lead and antimony. To describe the slag phase, the thermodynamic properties of at least four component oxides solutions: SiO₂-Bi₂O₃-Sb₂O₃-PbO should be known. It should be emphasised that there is no information on this subject in the existing literature. Consequently, the only quick solution is to combine required description according to selected simple thermodynamic model using the data for six binary systems. In our previous paper we reported optimized thermodynamic properties for PbO-SiO₂, PbO-Sb₂O₃, Sb₂O₅-SiO₂ and PbO-Sb₂O₃-SiO₂ liquid solutions [2]. In order to expand our knowledge about liquid binary silicate systems further, in this paper we attempted to determine thermodynamic properties of Bi₂O₃-SiO₂ liquid solution and to derive thermodynamic description of this binary phase diagram.

In the binary Bi₂O₃-SiO₂ system, three compounds, with Bi₂O₃:SiO₂ molar ratio = (6:1) (Bi₄Si₃O₁₂), (2:3) (Bi₁₂SiO₂₀) and (1:1) (Bi₃Si₃O₁₂) have been identified, and crystal structure data confirmed the existence of Bi₂O₃-SiO₂ (sillenite) and 2Bi₂O₃·3SiO₂ (eulytite) stable phases [3, 4]. In this paper the stable and metastable solid phases Bi₁₂SiO₂₀, Bi₃Si₃O₁₂ and Bi₂SiO₅ were denoted according to mole composition: (6:1), (1:1) and (2:3), respectively.

The first version on the Bi₂O₃-rich part of Bi₂O₃-SiO₂ phase diagram was suggested by Levin and Roth [5] and later such diagram was also published by Hill and Brice [6] and Takamori [7]. An equilibrium phase diagram was also proposed by Speranskaya et al. [8].

The equilibrium phase structures at the Bi₂O₃-rich side of the binary Bi₂O₃-SiO₂ system were first investigated by Levin and Roth [5] using high temperature XRD (X-Ray Diffraction). From the chemical analysis of bismuth silicate crystals Hill and Brice [6] suggested a narrow solid-solution range from 0.142 to 0.145 mole fraction of SiO₂. Later Takamori [7] showed a little wider range of 0.14 to 0.15 SiO₂ mole fraction. He obtained a single endothermic peak of melting at DTA (Differential Thermal Analysis) thermographs in this concentration range.
dark conductivity that allows a build-up of large spectrometry the activities of Bi2O3 in Bi2O3-SiO2 (6:1) is a very efficient photoconductor with low different physical properties [17]. Bismuth silicate (6:1) compound shows a unique combination of metastable phase equilibria in Bi2O3-SiO2 system. They also suggested congruent melting of (2:3) compound and a eutectic reaction with separation of SiO2 and (2:3) phase. Tananaev et al. [9] reported also appearance of some kinetically favored metastable phases at a high cooling rate (> 50 K/min).

In 1991 Kargin et al. [10] had reviewed stable and metastable phase equilibria in Bi2O3-SiO2 system basing on the available literature data. Using thermogravimetric and thermoelectric methods Shimanski [11] has studied the oxygen nonstoichiometry of bismuth silicate (6:1). He estimated maximum nonstoichiometry y = 0.003 for Bi12SiO20 at 973 K (700°C).

According to the DTA and XRD analysis Fei et al. [12] published stable and metastable phase diagrams. The first one was obtained from 10 K/min heating cycles. Since the silicate systems tend to supercool strongly, the cooling curves effects were used to determine also a metastable system. In the results obtained by Fei et al. [12, 13] one can notice the inconsistency in the stability of (2:3) compound. They reported both congruent melting of (2:3) phase at 1298 K (1025°C) from quenching and the peritectic reaction at 1303 K from DTA.

The experimental results of polymorphic transformations and invariant reactions in Bi2O3-SiO2 system found in the literature are summarized in Table 1.

Solid-state reactions in Bi2O3-SiO2 system were studied by DTA and XRD by Wang et al. [14]. Treating the mixture of Bi2O3 and SiO2 under different reaction time-temperature conditions, the metastable state compound Bi2SiO5 was observed. When temperature rises from 973 K to 1173 K (700-900°C) the transformation of (6:1) into (2:3) was found.

The crystallization kinetics and phase transformation of glass ceramics of mole ratio Bi2O3:SiO2 = 2:3 and the mechanism of homogeneous crystallization of single (6:1) crystals were studied by Guo et al. [15]. The thermodynamic properties of silicate glasses and melts were studied by Stolyarova et al. [16]. By use of differential high temperature mass spectrometry the activities of Bi2O3 in Bi2O3-SiO2 glasses at 1000 K (723°C) were determined.

It is worth to mention that the single crystal of (6:1) compound shows a unique combination of different physical properties [17]. Bismuth silicate (6:1) is a very efficient photoconductor with low dark conductivity that allows a build-up of large photo-induced space-charges. The (6:1) crystal is used in number of optical applications e.g. as wave mixing systems, spatial light modulators, optical correlators, laser systems for adaptive corrections of ultrashort light pulses and recording devices of dynamic real-time holograms [18, 19]. The fabrication of sillenite oxide thin-film crystal structures by different technique permits the development of a long list of devices including optical waveguides and integrated optical devices. Recently, the enhancement in photocatalytic activity of (6:1) nanofibers was reported by Batool et al. [20].

Table 1. Experimentally obtained and calculated polymorphic transformations and invariant reactions in Bi2O3-SiO2 system. L is the liquid phase, while α and δ phases respectively have monoclinic and fcc structure. SiO2 is a tridymite phase.

| Reaction | Temperature /K (°C) | Composition of liquid phase, xSiO2 | Literature |
|----------|---------------------|-----------------------------------|------------|
| α-Bi2O3 ↔ δ-Bi2O3 | 1003 (730) | - | [5, 7, 8, 10, 13] |
| L ↔ δ-Bi2O3 + (6:1) | 1002 (729) | - | This work |
| L ↔ Bi2O3 + (6:1) | 1096 (823) | 0.003 | This work |
| (6:1) ↔ L | 1173 (900) | 0.143 | [5] |
| L ↔ (6:1) + (2:3) | 1143 (870) | 0.245 | [8] |
| L ↔ (6:1) + u0 | 1143 (870) | 0.330 | [10] |
| u0 ↔ u0* | 1158 (885) | 0.250 | [13] |
| (2:3) ↔ L | 1142 (869) | 0.291 | This work |
| L ↔ (6:1) + u0 | 1148 (875) | -0.26 | [7] |
| u0 ↔ u0* | 1128 (855) | - | [7] |
| (2:3) ↔ L | 1293 (1020) | 0.60 | [8] |
| L ↔ (2:3) + SiO2 | 1298 (1025) | 0.60 | [13] |
| L + SiO2 ↔ (2:3) | 1303 (1030) | -0.60 | [13] |

* unidentified phases by Takamori [7] – polymorphic transformation suggested.
In turn, it is well known that bismuth silicate (2:3) is a good scintillation material [21, 22] due to its faster decay time (0.1 μs) and higher radiation hardness than that of classical bismuth germanate, Bi₄Ge₃O₁₂. It was also reported to show dielectric, pyroelectric, nonlinear optical, and possible ferroelectric effects based on its non-centrosymmetrical crystal structure [3, 13].

The third (1:1) bismuth silicate compound was identified to be metastable [23, 24]. It exhibits dielectric, pyroelectric, nonlinear optical effects, etc. and has non-centrosymmetrical crystal structure which may cause ferroelectric effect [25].

No thermodynamic data are known to exist for a liquid solution. Also, the complete phase relations and crystallizing behavior of the Bi₂O₃-SiO₂ system are still not explicitly known. Thus, except for thermodynamic properties of the liquid phase, it is important to develop the consistent descriptions of the phase relations to learn about crystallization behaviour of solid phases in the Bi₂O₃-SiO₂ system.

Consequently, in this work, attempts have been made to develop the consistent description of the phase relations in Bi₂O₃-SiO₂ system on the basis of determined thermodynamic properties.

2. Experimental.

2.1. E.m.f. measurements

2.1.1. Materials

Pure bismuth was obtained from Fluka AG (Switzerland) and was 99.9 % pure. The bismuth sesquioxide of 99.9% purity was obtained from POCh Gliwice (Poland). The amorphous silica powder of initial purity of 96.5% (POCh Gliwice, Poland) was ground and boiled in nitro-hydrochloric acid (Aqua regia). After drying and annealing the powder at 1250 K it was quickly quenched in the cold demineralised water. Finally, after another drying, fine SiO₂ powder (~99%) was obtained. In next step it was used in the sample preparation.

The weighed amounts of SiO₂ and Bi₂O₃ were mixed and then pelletized into cylindrical, small disks. These oxide pellets were placed on the top of Bi metal at a bottom of yttria-stabilized zirconia one-end closed electrolyte tubes of 400 mm length and 8 mm outside diameter (Yamari Trading Co., Japan). The melt of liquid metal and oxides was used as a working electrode of the experimental cell.

Solid phases 1:1 and 2:3 were prepared using sol-gel method. After diluting Bi(NO₃)₃· 5H₂O in distilled water with HNO₃ addition (until it completely dissolved), the resulting solution was mixed with appropriate amount of aerosil and sol (3% TEOS i.e. Si(OC₂H₅)₄) to obtain the required compositions with 1:1 and 2:3 mole ratio for both silicates. Solutions were first dried and next fired in air with increasing temperature step by step until 1000 K was reached. Then, samples were kept at this temperature for one hour and next cooled. XRD (X-Ray Diffraction) study (MiniFlex II, CuKα irradiation, Rigaku, Japan) confirmed the formation of respective phases. The sample purity was estimated to be not worse than 96.5% because the sample mass was not changed and no traces of reaction of the oxide samples with platinum crucible was observed.

2.1.2. Technique

E.m.f. cell, which was used in our experiments is shown, in Figure 1. The 2 g mass of metallic bismuth and the pellet of the oxide mixture of a chosen composition were placed in the tube of YSZ electrolyte. Dry air flushing the electrolyte tube from the outside acts as a reference electrode. It flowed in the outer furnace compartment. The outer part of the end of electrolyte tube was wrapped with platinum wire used as a reference electrode lead. The purified argon flowed inside the electrolyte tube acts as a protection of working electrode. Kanthal with welded tip of iridium wire was used as a lead to working electrode (Fig. 1).

![Figure 1. The schema of the e.m.f. cell used in this measurements with air reference electrode (P_02 = 0.213 bar)](image-url)
The temperature of the designed system was controlled by Eurotherm 815 controller (Eurotherm Ltd., United Kingdom). The high-resistance multimeter Keithley 2000 (Tektronix, Inc., USA) was adopted to electromotive force measurements. The e.m.f. vs. time variation at system equilibrium was controlled by the computer program written in Delphi 4.0. The experimental cell was working continuously for about one week. The measurements were taken for 0.2, 0.3, 0.4, 0.5, 0.55 and 0.75 mole fractions of SiO\(_2\) in cycles of increasing and decreasing temperature in the temperature range 1073-1293 K (800-1020°C).

### 2.2 DTA analysis

The (2:3) oxide was prepared from Bi\(_2\)O\(_3\) (99.9%) obtained from POCh Gliwice (Poland) and SiO\(_2\) powder obtained in the process described in [26] for heat capacity measurements. After weighing the appropriate amounts of SiO\(_2\) and Bi\(_2\)O\(_3\), the oxide mixture was pelleted by cold pressing into small disks of 1.5 mm thickness and 5 mm diameter. The samples were prepared by double sintering on platinum plate in air at 1223 K during 30 h with intermediate grinding in agate mortar and second cold pressing. The purity of sample was estimated to be not worse than 96.5% because after synthesis no change of sample mass was observed. The X-ray diffractometer (XRD, MiniFlex II, CuK\(_\alpha\) irradiation, Rigaku, Japan) was used for the determination of the sample pellets crystal structure. The diffraction results revealed the (2:3) silicate crystal structure (JCPDS Card No. 35-1007). The homogenous polycrystalline structure of Bi\(_2\)Si\(_2\)O\(_6\) compound was revealed from back scattered electrons (BSE) micrographs (Hitachi, S-3400N, Japan) [26] and EDX (Energy Dispersive X-ray) analysis.

The measurements were performed on high quality DSC apparatus Pegasus 404 F1 from NETZSCH (Germany) working in DTA mode. The symmetrical sample carrier was designed to keep two crucibles, one for the tested sample and another for the reference sample. To establish an internal calibration file, the DTA sensor was calibrated for the reference sample. To establish an internal calibration file, the DTA sensor was calibrated for the reference sample. To establish an internal calibration file, the DTA sensor was calibrated for the reference sample. To establish an internal calibration file, the DTA sensor was calibrated for the reference sample. The measurements were taken for 0.2, 0.3, 0.4, 0.5, 0.55 and 0.75 mole fractions of SiO\(_2\) in cycles of increasing and decreasing temperature in the temperature range 1073-1293 K (800-1020°C).

### 3. Results

#### 3.1 Thermodynamic properties of Bi\(_2\)O\(_3\)-SiO\(_2\) liquid solutions

In order to determine Bi\(_2\)O\(_3\) activity in the liquid slag, at the beginning of our experiments Gibbs energy of formation of pure solid and liquid Bi\(_2\)O\(_3\) according to the reaction:

\[ 2\text{Bi} + \frac{3}{2}\text{O}_2 = \text{Bi}_2\text{O}_3 \]

was determined. The galvanic cell of the type:

\[ \text{Ir, Bi} | \text{Bi}_2\text{O}_3(\text{s},\text{l}) | \text{O}^+ | \text{air, Pt} \]

was employed in the temperature range from 1073 to 1293 K (800-1020°C).

Gibbs free energy of formation was calculated from the following expression:

\[ \Delta G_{\text{Bi}_2\text{O}_3} = -6 FE_\text{Ir} + 3/2 R T \ln p_\text{O}_2 \]

where: \( T \) is a absolute temperature, \( R \) and \( F \) are gas constant and Faraday constant, respectively. Finally, \( E_\text{Ir} \) is an electromotive force of cell (I) and \( p_\text{O}_2 \) denotes the oxygen partial pressure at the air reference electrode (0.213 bar). In this work all obtained e.m.f. values of experimental cells were corrected with thermo electromotive force of (Kanthal+Ir)–Pt junction [27]:

\[ E_{\text{Kanthal}-\text{Ir} - \text{Pt}}(V) = 2.363 \times 10^{-4} + 5.458 \times 10^{-7} T - 8.32 \times 10^{-3} \]

No temperature difference between Kanthal-Iridium tip junction and the sample was accepted.

After correction the results of measurements were treated by least-squares analysis and resulting equations as the \( E(T) \) functions are given in Table 2. Gibbs free energy of formation of liquid bismuth sesquioxide was derived directly from eq. (2) and is given in the following form:

\[ \Delta G_{\text{Bi}_2\text{O}_3} \text{(J mol}^{-1} \text{)} = -522350 (±1640) + 235.63 (±20.85) T \]

This result was compared in Fig. 2 with earlier published experimental data [28-33]. The scatter of the data is ~2.5% of measured value and in case of Ganesan et al. [32] comprehensive review is even <0.5%. In consequence, it can be supposed that the determination of thermodynamic properties of oxide system by use of our experimental setup is reliable and accurate.

Next, the following cell II:

\[ \text{Ir, Bi} | \text{(Bi}_2\text{O}_3)_x | (\text{SiO}_2)_y | \text{O}^+ | \text{air, Pt} \]
was used to measure Bi$_2$O$_3$ activity in the liquid slags.

The e.m.f. results of cell II, $E_{II}$, together with least-squares fit are collected Table 2 and shown in Fig. 3 as a function of SiO$_2$ mole fraction.

For the overall cell reaction (1) taking place in cell II, the change of Gibbs free energy can be given as:

$$
\Delta G = -6FE_{II} = \Delta G^°_{f,Bi_2O_3} + RT \ln a_{Bi_2O_3} - RT \ln p_{O_2} \tag{4}
$$

Combining equations (2) and (4) the following dependence for the ln $a_{Bi_2O_3}$ can be derived:

$$
RT \ln a_{Bi_2O_3} = 6F(E_i - E_{II}) \tag{5}
$$

Activities of bismuth sesquisoxide were obtained directly from measured e.m.f.’s with the use of eq. (5). Obtained results shows negative deviation from the Raoult’s law which is compatible with the formation of solid oxide compounds in this binary system.

Attempts have also been made to determine thermodynamic stability of solid 1:1 and 2:3 phases. Two cells of the type:

- Bi (SiO$_2$ + 2:3) | YSZ, O$^{2-}$ | air and
- Bi (2:3 + 1:1) | YSZ, O$^{2-}$ | air

were assembled. Composition of prepared electrodes corresponded to silica mole fraction $x_{SiO_2} = 0.55$ and 0.75, respectively. However, it was observed that the cell did not work reproducibly, e.m.f. results were scattered, and the resistance of the cell was unusually high. Thus, these attempts failed to provide any reliable data. Nevertheless, above 1200 K, e.m.f.’s were stabilized and demonstrated similar trends as those obtained for the cell II. It was assumed that above 1200 K samples were liquid. The results obtained from cells III and IV were not taken into consideration.

3.2. Heat capacity temperature dependence.

The heat capacity data for two (6:1) and (2:3) bismuth silicate compounds obtained by Onderka [26] in the temperature range from 330 to 1135 K were accepted for the determination of Gibbs free energy of bismuth silicates. The details of the experimental procedure and $C_v(T)$ estimation are given in the previous paper [26]. The temperature dependence for respective phases determined in the temperature range from 298 to 1135 K has the form of three-term Maier-Kelley polynomial representation, $a + bT + cT^2$ [34]:

(6:1) phase: $C_v(T) = 783.2 + 0.10501 \cdot T - 1.5768698 \cdot 10^7 \cdot T^{-2} \cdot (J/mol \cdot K^{-1})$ \tag{6}

(2:3) phase: $C_v(T) = 443.5 + 5.743 \cdot 10^2 \cdot T - 9.80545 \cdot 10^6 \cdot T^{-2} \cdot (J/mol \cdot K^{-1})$ \tag{7}
The standard entropy, $S_{\text{std}}^{0}$, of bismuth silicates (6:1) and (2:3) were calculated as 15.7±2.2 J/mol atoms·K$^{-1}$ and 13.9±1.5 J/mol-atoms·K$^{-1}$, respectively. The low-temperature heat capacities [26] were estimated by adoption of the modified Debye function [35] and the obtained dependencies (6, 7) were accepted for phase diagram calculations.

3.3. DTA measurements

On DTA diagram for the (2:3) phase composition (Fig. 4) two characteristic onset temperatures were recorded: one at 1156.3 K (883.2°C), and the second at 1280.6 K (1007.5°C), respectively. It may suggest that this phase was not 100% pure, but it was rather a mixture of two phases. Taking into account the way of preparation the possible traces of bismuth oxide can be assumed. Consequently, the first peak may correspond to eutectic mixture formation: $L \leftrightarrow (6:1)+(2:3)$, while the second is characteristic for crossing the invariant tie-line of peritectic reaction: $L+\text{SiO}_2 \leftrightarrow (2:3)$. Since, the liquid phase composition of such reaction is close to the composition of (2:3) compound, the thermal signal of liquidus was not detected on this thermogram.

The only onset temperature detected during cooling cycle of this sample is close to the temperature of melting of (1:1) compound which was estimated at 1123 K (850°C) and 1118 K (845°C) from 10 K/min cooling part of DTA curves by Kargin et al. [10] and Fei et al. [13], respectively. It was shown in literature [10, 13] that thermal effects in this system strongly depend on sample thermal history.

In case of sample of $x_{\text{Bi}_2}$ = 0.7 upon heating, the endothermic effects were detected at 1154.1 K (881°C), 1281 K (1008°C) and 1442.1 K (1169°C). First onset temperature can be (as in case of (2:3) sample) assigned to eutectic reaction: $L \leftrightarrow (6:1)$ + $\text{Bi}_2\text{O}_3$.

![Figure 4](image1.png)

**Figure 4.** DTA heating and cooling cycles results for (2:3) compound recorded at 5 K/min rate.

![Figure 5](image2.png)

**Figure 5.** DTA heating and cooling cycles results for sample concentration $x_{\text{Bi}_2} = 0.7$ recorded at 5 K/min rate.
(2:3). Additionally, the exothermic peak at 1176.6 K was observed, which can be interpreted as the evidence of a reaction of amorphous SiO₂ with the not detectable by XRD traces of Bi₂O₃ and formation of (2:3) bismuth silicide. Fei et al. [13] observed at 1158 K (885°C) the formation of (2:3) phase during heating of the starting material of equimolar composition of Bi₂O₃ and SiO₂. This sample melted at 1286 K (1013°C). They also observed the crystallization of melted (1:1) sample upon cooling at 1118 K (845°C) with significant supercooling. The same melting and crystallizing behaviour was observed for re-heating and re-cooling cycles.

The second and third onset temperatures of the endothermic effects can be associated with incongruent melting of (2:3) compound and liquidus temperature. The obtained experimental values of thermal effects both for heating and cooling, are listed in Table 3 and shown in Fig. 5.

It seems that faster heating rates can give the results of greater inconsistency because of the strong tendency of glass formation in this oxide system. Additionally, Fei et al. [37] concluded that although BSO melts near-congruently at 1298 K (1025°C) in the stable phase equilibrium, its melt tends to supercool strongly and crystallizes in accordance with the metastable phase diagram forming (1:1) compound. Despite, the fact that (1:1) compound is a metastable phase compound it can crystallize out in a wide range of concentration in Bi₂O₃-SiO₂ system and can be cooled to room temperature without any phase transition. During Bridgman growth it was observed that without crystal seed only (1:1) compound crystallized from the melt of (2:3) composition at about 1123 K (850°C). Additionally, Denisov et al. [38] measured the heat capacity of the (1:1) compound in the temperature range between 380 K and 1000 K with different heating rates. Dimitriev et al. [36] during sol-gel synthesis observed the beginning of the crystallisation with separation of (1:1) and (2:3) compounds from the amorphous matrix in the temperature range 673-873 K (400-600°C).

### Table 3. DTA results obtained with DSC/DTA apparatus during cooling and heating cycles.

| x₂O₁₂ | x₅O₂ | Thermal arrests / K (°C) |
|-------|------|-------------------------|
|       |      | heating                 |
| 0.4   | 0.6  | 1156.3 (883.2)o, 1280.6 (1007.5)o, 1297.2 (1024.1)p |
| 0.3   | 0.7  | 1154.1 (881.0)o, 1176.6 (903.5)p, 1281 (1007.9)o, 1442.1 (1169)p |
|       |      | cooling                 |
| 0.4   | 0.6  | 1117.3 (844.2)e         |
| 0.3   | 0.7  | 1121.9 (848.8)e         |

o – onset, e – endset and p – peak

4. Optimization of the Phase Diagram

To describe the oxide liquid phase a substitutional solution model was applied. The Gibbs free energy of one mole of an oxide solution is expressed in the form:

\[ G_\text{m} = x_{\text{Bi}_2\text{O}_3}G_\text{m}_{\text{Bi}_2\text{O}_3} + x_{\text{SiO}_2}G_\text{m}_{\text{SiO}_2} + \]

\[ + RT \left( x_{\text{Bi}_2\text{O}_3} \ln x_{\text{Bi}_2\text{O}_3} + x_{\text{SiO}_2} \ln x_{\text{SiO}_2} \right) + \Delta G_\text{m} \]  

(8)

where: \( T \) is a temperature (in Kelvin), \( R \) is a gas constant, \( x_{\text{Bi}_2\text{O}_3} \) and \( x_{\text{SiO}_2} \) are the molar fractions of Bi₂O₃ and SiO₂, respectively.

The parameter \( G_\text{m} \) is the Gibbs free energy of pure oxides \( i \), i.e. Bi₂O₃ and SiO₂. To ensure the compatibility with subsystem assessments of Bi-Pb-Sb-Si-O system, the values of Gibbs energies for Bi₂O₃ and SiO₂ were used from [39] and [40], respectively. The Redlich-Kister equation [41] was taken to express the excess Gibbs free energy, \( \Delta G_\text{m} \), of substitutional solution:

\[ \Delta G_\text{m} = x_{\text{Bi}_2\text{O}_3}x_{\text{SiO}_2} \sum_{i=0}^{p+q} x_{\text{Bi}_2\text{O}_3} x_{\text{SiO}_2}^{i+q} L_{\text{Bi}_2\text{O}_3,\text{SiO}_2}^{i} \]  

(9)

where the interaction parameters \( L_{\text{Bi}_2\text{O}_3,\text{SiO}_2}^{i} \) are temperature dependent and given in J·mole⁻¹. All thermodynamic functions for the liquid solutions can be calculated directly from Eq. (10):

\[ G^p(T) - H^{\text{ex}} = A + BT + CT \ln(T) + \]

\[ + DT^2 + ET^3 + FT^{-1} \]

\[ = H + BT + CT \ln(T) + \]

\[ + DT^2 + ET^3 + FT^{-1} \]  

(10)

where \( H^{\text{ex}} \) refers to \( H^0 \) (298.15) and \( p, q \) are the number of moles of Bi₂O₃ and SiO₂, respectively.

The four coefficients \( C, D, E \) and \( F \) can be directly determined by comparing the representation of the experimental heat capacity (eq. 6 and 7), \( C_p \) with equation calculated directly from Eq. (10):

\[ C_p(T) = -C - 2DT - 6ET^2 - 2FT^2 \]  

(11)

where in present analysis the parameter \( E \) is equal zero.
Essentially, the other two coefficients, $H$ and $B$ (eq. 10), can be evaluated from the standard enthalpy of formation $\Delta H^0_f$ and the absolute entropy $S^0_{298}$. Because of the lack of data, the values of $H$ (in eq. 10) were optimized during thermodynamic modelling by taking into account all the thermodynamic data and the phase equilibrium data. In order to fit the phase equilibrium data associated with the bismuth silicate phases, parameters $B$ were not evaluated directly from $S^0_{298}$, but optimized during thermodynamic modelling.

Using thermodynamic description of the liquid phase (8, 9), heat capacity of both silicates [23], and available data on phase equilibria [5, 7, 8, 10, 13] and present work (Tab. 3), as well as the activity data obtained in this study, the binary Bi$_2$O$_3$-SiO$_2$ system was assessed. According to obtained thermodynamic parameters (Tab. 4) the phase diagram was calculated and is shown in Fig. 6. The nonstoichiometry of (6:1) compound was not taken into account.

The comparison between calculated and experimentally obtained Bi$_2$O$_3$ activities in liquid oxide solution is shown in Fig. 7 at 1073 and 1273 K (800 and 1000°C). The negative deviations from ideal behaviour were revealed for melt composition in the Bi$_2$O$_3$ rich part of the system. The negative deviation of the activities of Bi$_2$O$_3$ in Bi$_2$O$_3$-SiO$_2$ glasses at 1000 K (723°C) was also observed by Stolyarova et al. [16] during differential high temperature mass spectrometry measurements.

In the present modelling, only the parameters of the liquid and the coefficients $H$ and $B$ for phases (6:1) and (2:3) were allowed to be adjusted. The thermodynamic evaluation was conducted by the optimization and calculation with the computer-operated programs, TCCS (ThermoCalc AB, Sweden) [42] and Pandat 8.1 (Computherm LLC, USA) [43, 44].

### Table 4. Optimized model parameters of the phases in the Bi$_2$O$_3$-SiO$_2$ system.

| Parameter | Assessed parameters, $T$ | Liquid phase | Substitutional model |
|-----------|--------------------------|--------------|----------------------|
| $L_{PbO,SiO_2}$ | $-12141.0 - 6.7821 \cdot T / J \cdot \text{mole}^{-1}$ | | |
| $L_{PbO,SiO_2}$ | $-44006.9 + 15.9228 \cdot T / J \cdot \text{mole}^{-1}$ | | |
| $L_{PbO,SiO_2}$ | $+45441.3 - 18.1458 \cdot T / J \cdot \text{mole}^{-1}$ | | |
| Phase Bi$_2$SiO$_5$ | Line compound | | |
| $G_{J, Bi_2SiO_5}$ | $-679163.5 + 635.5743 \cdot T / J \cdot \text{mol at.}$ | | |
| Phase Bi$_4$Si$_3$O$_12$ | Line compound | | |
| $G_{J, Bi_4Si_3O_12}$ | $-843273.9 + 540.4287 \cdot T / J \cdot \text{mol at.}$ | | |

Reference: [42] and Pandat 8.1 (Computherm LLC, USA) [43, 44].

### 5. Conclusions

In the present paper the phase diagram of pseudobinary Bi$_2$O$_3$-SiO$_2$ oxide system has been assessed. The important conclusions can be drawn from the obtained results:

- Determined from electromotive force measurements Gibbs energy of formation of pure Bi$_2$O$_3$ oxide, $\Delta G^0_{f, Bi_2O_3}$, is in good agreement with the literature data. This result can be treated as a test of a good precision of conducted experiments and the reversibility of cell operation. This fact and the reversible work of our cell ensure that the possible side reactions due to reactivity of oxide liquid phase were in this cell under control.

- Measured activities of bismuth sesquioxide in liquid Bi$_2$O$_3$-SiO$_2$ solutions showed negative
deviations from the Raoult’s law. Experiments were difficult due to the strong tendency of the melt to undercooling and glass formation.

- Even minimal quantity of the experimental data allows prediction of unknown phase diagram by CALPHAD method.

- Finally, assessed parameters of the liquid Bi$_2$O$_3$-SiO$_2$ solution can be used to describe the oxide liquid phase of quaternary Bi$_2$O$_3$-PbO-Sb$_2$O$_3$-SiO$_2$ system, contributing to the database for calculations of thermodynamic properties of the liquid slags occurring in Kaldo process.

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