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Thermochemical and thermodynamical properties of 14 complex oxides in the SrO–Bi_2O_3 system[1]

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Abstract

The known data for the phases $Sr_6Bi_2O_9$, $Sr_3Bi_2O_6$, $Sr_2Bi_2O_5$, $Sr_{18}Bi_{22}O_{51}$, $Sr_6Bi_{14}O_{27}$, $SrBi_4O_7$, $Sr_2Bi_6O_{11}$, $SrBi_2O_4$, $Sr_8Bi_{10}O_{23}$, $Sr_8Bi_2O_{11}$, $Sr_5Bi_6O_{14}$, $Sr_6Bi_2O_{11}$, $Sr_6Bi_4O_{15}$ and $Sr_{24}Bi_{14}O_{52}$ have been revised and corrected, unknown data have been estimated. The values of ΔH^0_{298}, S^0_{298}, H^0_{297}-H^0_0, the T and ΔH values for the phase transformations, $C_p(T)$ for the crystalline state, C_p at $T > T_{\text{ph.tr}}$, and also the polynomial approximating a reduced Gibbs are presented.

Keywords: Complex oxide; Properties; Calculation

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1. Introduction

The properties of double oxides in the SrO–Bi_2O_3 system are of interest in connection with the synthesis of ceramic superconductors in the SrO–Bi_2O_3–CuO system. These oxides can also be considered as materials for other purposes.

According to Refs. [1–5], the following double oxides can also exist in the SrO–Bi_2O_3 system: $Sr_6Bi_2O_9$, $Sr_3Bi_2O_6$, $Sr_2Bi_2O_5$, $Sr_{18}Bi_{22}O_{51}$, $Sr_6Bi_{14}O_{27}$, $SrBi_4O_7$, $Sr_2Bi_6O_{11}$, $SrBi_2O_4$, $Sr_8Bi_{10}O_{23}$, $Sr_8Bi_2O_{11}$, $Sr_5Bi_6O_{14}$, $Sr_6Bi_2O_{11}$, $Sr_6Bi_4O_{15}$ and $Sr_{24}Bi_{14}O_{52}$.

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[1] Dedicated to Takeo Ozawa on the Occasion of his 65th Birthday.

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All the oxides, except $Sr_6Bi_2O_{11}$, $Sr_6Bi_4O_{15}$ and $Sr_{24}Bi_{14}O_{52}$, can be described according to a common formation reaction

$$x\,SrO + y\,Bi_2O_3 = Sr_xBi_{2y}O_{x+3y} \tag{1}$$

where x and y are the number of moles of simple oxides in the complex oxide.

For three oxides the number of oxygen atoms in the compounds are more than the number given by reaction (1). Their formation can be described by a combination of reactions (1) and (2)

$$Sr_xBi_{2y}O_{x+3y} + n_0O_2 = Sr_xBi_{2y}O_{x+3y+n_0O_2} \tag{2}$$

where n_0 is the number of surplus oxide moles.

The literature data (Table 1) are not complete: H^0_{298} for 6 phases [3], and the temperatures and types of phase transformation for 5 phases [5–7] are available.

The goal of this work is the revision and correction of known data, estimation of the unknown thermochemical properties of the above-mentioned phases, and also the transformation of the information obtained into a form suitable for application in thermodynamic simulations [8]. These problems have been solved using known data on complex oxides [2–7], simple oxides [9], various calculation methods [10, 11], and the program ASTRA - 4 [12].

Table 1
Known thermochemical properties of some complex oxides in the $SrO–Bi_2O_3$ system

Oxide	Standard enthalpy of formation according to Ref. [3]			T of phase transformation in K and type of transformation
	ΔH^0_{298}/kJ mol^{-1} from elements	ΔH^0_{298}(ox)/kJ mol^{-1} from simple oxides	$H^0_{at}(f)^a$ ΔH^0_{298}(ox)/n/kJ (g atom)$^{-1}$	
$Sr_6Bi_2O_9$	−4668.0	−540.6	−31.8	1250, DCS [6] 1238, DCS [7]
$Sr_6Bi_2O_6$	−2470.0	−104.5	−9.5	1263, DCS [5], 1253, DCS [6] 1483 IM [7]
$Sr_2Bi_2O_5$	−1885.2	−115.2	−12.8	1210, DCS [5], 1223, DCS [6] 1213, IM [7]
$Sr_{18}Bi_{22}O_{51}$	−17968.0	−882.7	−9.7	–
$Sr_6Bi_{14}O_{27}$	−8132.0	−441.8	−9.4	–
$SrBi_4O_7$	−1797.0	−57.6	−4.8	–
$SrBi_2O_4$	–	–	–	1063, DCS [5], 1213, IM [7]
$Sr_5Bi_6O_{14}$	–	–	–	1213, CM [5]

[a] In Ref. [3], this value is marked as ΔH_R.

Key: DCS, IM and CM represent decomposition in the crystalline state, and incongruent and congruent melting, respectively

2. Revision, correction and calculation of properties

2.1. *Standard enthalpies of formation (SEF),* ΔH^0_{298}

For all double oxides, except $Sr_6Bi_2O_{11}$, $Sr_6Bi_4O_{15}$ and $Sr_{24}Bi_{14}O_{52}$ the ΔH^0_{298} values were calculated using the equation

$$\Delta H^0_{298}(j) = \sum n_i \Delta H^0_{298}(i) + \Delta H^0_{298}(\mathrm{ox})_j \quad (\mathrm{kJ\,mol^{-1}}) \tag{3}$$

where n_i is number of the ith simple oxide in the jth double oxide $\Delta H^0_{298}(i)$ is the SEF of the ith simple oxide and $\Delta H^0_{298}(\mathrm{ox})_j$ is the SEF of the jth double oxide from simple oxides. The first member of Eq. (3) was calculated on the basis of oxide composition and reference data [9]. The analysis and estimation of the $\Delta H^0_{298}(\mathrm{ox})_j$ values were carried out using the following various methods.

2.1.1. *With application of the data [3] and empirical dependence [13]*

Experimental $\Delta H^0_{298}(\mathrm{ox})$ values for 6 double oxides [3] (in kJ (g atom)$^{-1}$, Table 1) were revised and corrected with the help of the linear approximation rule (LAR) for related double inorganic compounds [13]

$$H^0_{\mathrm{at}}(f)_j = \Delta H^0_{298}(\mathrm{ox})_j/n_j \quad (\mathrm{kJ\,(g\,atom)^{-1}}) \tag{4}$$

where $H^0_{\mathrm{at}}(f)_j$ is the SEF of the jth double oxide from simple oxides presented in kJ (g atom)$^{-1}$, and n_j is the number of atoms in a molecule of double oxide

$$\tilde{H}^0_{\mathrm{at}(j)} = \sum x(i)\, H^0_{\mathrm{at}}(i) \quad (\mathrm{kJ\,(g\,atom)^{-1}}) \tag{5}$$

where $x(i)$ is the molar fraction of the ith simple oxide in a jth double oxide, and $H^0_{\mathrm{at}}(i)$ is the SEF of the ith simple oxide (in kJ (g atom)$^{-1}$

$$H^0_{\mathrm{at}}(i) = \Delta H^0_{298}(i) n_i \quad (\mathrm{kJ\,(g\,atom)^{-1}}) \tag{6}$$

where n_i is the number of atoms in a molecule of ith simple oxide. The essence of the LAR is the dependence

$$H^0_{\mathrm{at}}(f)_j = f[H^0_{\mathrm{at}}(i), \tilde{H}^0_{\mathrm{at}}(j)] \quad (\mathrm{kJ\,(g\,atom)^{-1}}) \tag{7}$$

which for related double compounds has an $H^0_{\mathrm{at}}(f)_j$ minimum value. The $H^0_{\mathrm{at}}(f)_j$ values are described by linear equations between $H^0_{\mathrm{at}}(i)$ and $H^0_{\mathrm{at}}(f)_j$ (min) with average deviations from reference data of not more than ± 5% [13].

Results of the LAR application are shown in Fig. 1. It can be seen that the data [3], except $H^0_{\mathrm{at}}(f)$ for $Sr_6Bi_2O_9$ (point 2), agree satisfactorily with the LAR (average difference between linear dependences and experimental data [3] is ± 12.3%).

The linear equations for determining $H^0_{\mathrm{at}}(f)_j$ according to Ref. [13] are

$$H^0_{\mathrm{at}}(f)_j = -57.6746 - 0.1949\, \tilde{H}^0_{\mathrm{at}}(j) (\mathrm{kJ\,(g\,atom)^{-1}}) (\text{between points 1 and 4}') \tag{8}$$

$$H^0_{\mathrm{at}}(f)_j = 11.1032 + 0.09731\, \tilde{H}^0_{\mathrm{at}}(j) (\mathrm{kJ\,(g\,atom)^{-1}}) (\text{between points 4}' \text{ and 8}) \tag{9}$$

Eqs. (8) and (9) are consequently used for correction of known data and for calculation of unknown SEF data for the double oxides, see Table 2.

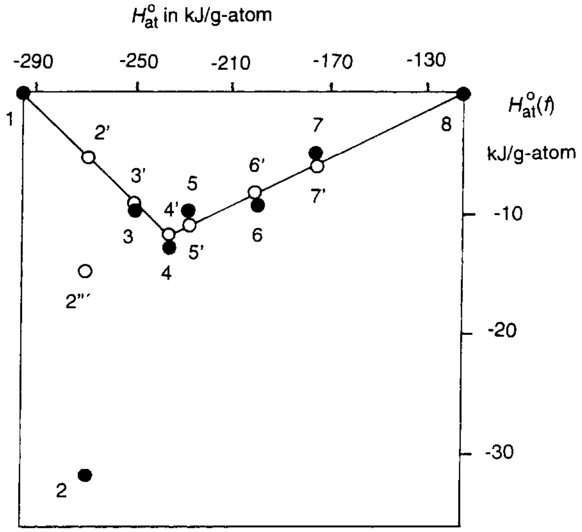

Fig. 1. Application of the linear approximation rule (LAR) [13] for the revision and correction of the standard enthalpies of formation from simple oxides $(H^0_{at}(f))_j$ in kJ (g atom)$^{-1}$ for some double oxides in the SrO–Bi_2O_3 system: 1 SrO [9]; 2, $Sr_6Bi_2O_9$ [3]; 3, $Sr_3Bi_2O_6$ [3]; 4, $Sr_2Bi_2O_5$ [3]; 5, $Sr_{18}Bi_{22}O_{51}$ [3]; 6, $Sr_6Bi_{14}O_{27}$ [3]; 7, $SrBi_4O_7$ [3]; and 8, Bi_2O_3 [9]. The $H^0_{at}(f)_j$ values based on the LAR for: 1, SrO; 2', $Sr_6Bi_2O_9$; 3' $Sr_3Bi_2O_6$; 4', $Sr_2Bi_2O_5$; $Sr_{18}Bi_{22}O_{51}$; 6', $Sr_6Bi_{14}O_{27}$; 7', $SrBi_4O_7$; and 8, Bi_2O_3. Point 2' corresponds to the ΔH_R ($Sr_6Bi_2O_{11}$) calculated by Eq. (28). It follows that $H^0_{at}(f)_j = -57.6746 - 0.1949\bar{H}^0_{at}(j)$ in kJ (g atom)$^{-1}$ between points 1 and 4'; and $H^0_{at}(f)_j = 11.1032 + 0.09731\,\bar{H}^0_{at}(j)$ in kJ (g atom)$^{-1}$ between points 4' and 8.

2.1.2. *According to the empirical dependence [14]*

$$\Delta H^0_{298}(\mathrm{ox})_j \simeq -29.274\,m_0(j) \quad (\mathrm{kJ\,mol^{-1}}) \qquad (10)$$

where m_0 is the number of oxide atoms in the complex oxide molecule. The results of calculation by Eq. (10) are given in Table 2. It can be seen that the differences between the calculated and experimental data are considerable, and they have a constant sign of deviation, except $Sr_6Bi_2O_9$. It is possible to conclude that the application of Eq. (10) carried out against more negative SEF values, and the associated numerical coefficient in Eq. (10) must be corrected. For this group of double oxides, the $\Delta H^0_{298}(\mathrm{ox})_j$ values calculated with the help of Eqs. (8) and (9) are taken as reliable (see Table 2). For $Sr_6Bi_2O_9$, the SEF according to Ref. [3] is considered erroneous.

2.1.3. *SEF values of $Sr_6Bi_2O_{11}$, $Sr_6Bi_4O_{15}$ and $Sr_{24}Bi_{14}O_{52}$*

First, the $\Delta H^0_{298}(\mathrm{ox})$ values for $Sr_xBi_{2y}O_{x+3y}$ calculated using Eqs. (8) and/or (9) were employed. Then ΔH^0_{298} values were determined taking into account Eq. (3). Finally, $\Delta H^0_{298}(Sr_xBi_{2y}O_{x+3y} + n_0)$ values were calculated using reaction (2). The molar enthalpy of joining n oxygen molecules (ΔH^0) is taken as 184 kJ (mol O_2)$^{-1}$ [15].

Table 2
Standard enthalpies of formation for 14 double oxides in the SrO–Bi_2O_3 system

	Oxide	Experimental data [3]		Corrected data taken as reliable		δ/% difference between corrected and experimental data	ΔH^0_{298} (ox) calculated by Eq. (10)/ kJ mol^{-1}	δ/% difference between calculated and experimental data	ΔH^0_{298}/kJ mol^{-1}		δ/% difference between taken as reliable and experimental data
		$H^0_{at}(f) = \Delta H_R$/ kJ (g-atm)$^{-1}$	H^0_{298}(ox)/ kJ mol^{-1}	$H^0_{at}(f)$ kJ (g-atom)$^{-1}$	ΔH^0_{298}(ox)/ kJ mol^{-1}				Taken as reliable	Experimental data [3]	
1	$Sr_6Bi_2O_9$	−31.8	−540.6	−5.067	−86.14	+84.1	−263.5	+51.5	−4207.44	−4668.0	+9.9
2	$Sr_3Bi_2O_6$	−9.5	−104.5	−8.864	−97.50	+6.7	+175.6	−68.0	−2443.40	−2470.0	+1.1
3	$Sr_2Bi_2O_5$	−12.8	−115.2	−11.800	−106.20	+7.8	−146.4	−27.1	−1860.30	−1885.2	+1.3
4	$Sr_{18}Bi_{22}O_{51}$	−9.7	−882.7	−11.0	−1001.0	−13.4	−1494.0	−69.1	−17928.90	−17968.0	+0.2
5	$Sr_6Bi_{14}O_{27}$	−9.4	−441.8	−8.155	−383.28	+13.2	−790.4	−78.9	−7927.58	−8132.0	+2.5
6	$SrBi_4O_7$	−4.8	−57.6	−5.89	−70.68	−22.9	−204.9	−255.7	−1803.48	−1797.0	−0.4
7	$Sr_2Bi_6O_{11}$	–	–	−7.062	−134.45	–	−322.0	–	−3029.55	–	–
8	$SrBi_2O_4$	–	–	−8.845	−61.92	–	117.1	–	−1224.22	–	–
9	$Sr_8Bi_{10}O_{23}$	–	–	−10.882	−446.16	–	−673.3	–	−8033.06	–	–
10	$Sr_8Bi_2O_{11}$	–	–	−3.935	−82.63	–	−322.0	–	−5387.53	–	–
11	$Sr_5Bi_6O_{14}$	–	–	−11.057	−232.20	–	−409.8	–	−4902.70	–	–
12	$Sr_6Bi_2O_{11}$	–	–	−5.067[a]	−86.14[a]	–	–	–	−4391.44	–	–
13	$Sr_6Bi_4O_{15}$	–	–	−8.860[a]	−194.92[a]	–	–	–	−5162.72	–	–
14	$Sr_{24}Bi_{14}O_{52}$	–	–	−8.010[a]	−360.45[a]	–	–	–	−19201.15	–	–

[a] Calculated by Eqs. (8) and (9) for $Sr_6Bi_2O_9$, $Sr_6Bi_{14}O_{12}$ and $Sr_{24}Bi_{14}O_{45}$ respectively.

Using $Sr_6Bi_2O_{11}$ as an example, the procedure is as follows

$$\begin{aligned}\tilde{H}^0_{\mathrm{at}} &= x(\mathrm{Sr})(-5[\Delta H^0_{298}(\mathrm{SrO})]/n_{\mathrm{SrO}} + x(\mathrm{Bi_2O_3})[\Delta H^0_{298}(\mathrm{Bi_2O_3})]/n_{\mathrm{Bi_2O_3}} \\ &= (6/7)(-591.8)/2 + (1/7)(570.5)/5 = -269.92\,\mathrm{kJ\ (g\ atom)^{-1}} \qquad (11)\end{aligned}$$

For $(Sr_xBi_{2y}O_{x+3y})$ or $Sr_6Bi_2O_9$, according to Eq. (8)

$$H^0_{\mathrm{at}}(f) = -57.6746 - 0.1949(-269.92) = -5.067\,\mathrm{kJ\ (g\ atom)^{-1}} \qquad (12)$$

and according to Eq. (6)

$$\Delta H^0_{298}(\mathrm{ox}) = H^0_{\mathrm{at}}(f)_j n_j = -5.067 \times 17 = -86.14\,\mathrm{kJ\ mol^{-1}} \qquad (13)$$

Then, with the help of Eq. (3)

$$\begin{aligned}\Delta H^0_{298}(\mathrm{Sr_6Bi_2O_9}) &= 6(-591.8) + 1(-570.5) + (-86.14) \\ &= -4207.44\,\mathrm{kJ\ mol^{-1}} \qquad (14)\end{aligned}$$

Finally, for $Sr_xBi_{2y}O_{x+3y+n_0}$ according to Eq. (2)

$$\begin{aligned}\Delta H^0_{298}(\mathrm{Sr_6Bi_2O_{11}}) &= \Delta H^0_{298}(\mathrm{Sr_6Bi_2O_9}) + 1.\Delta H_{\mathrm{O_2}} \\ &= -4207.44 + (-184.0) = -4391.44 \quad \mathrm{kJ\ mol^{-1}} \qquad (15)\end{aligned}$$

Results of calculations are given in Table 2.

For estimation of other properties of these oxides, we did not take into account the presence of surplus oxygen besides reaction (1). Consequently for $Sr_6Bi_2O_{11}$, $Sr_6Bi_4O_{15}$ and $Sr_{24}Bi_{14}O_{52}$, we proceed in the same way.

2.2. *Standard entropy*

Three methods have been used:

(i) The additivity method

$$S^0_{298}(j) \approx \sum n_i S^0_{298}(i) \quad (\mathrm{J\ K^{-1}\ mol^{-1}}) \qquad (16)$$

where n_i is the number of moles and $S^0_{298}(i)$ is the standard entropy of the ith simple oxide. (ii) The Gertz method [16]

$$S^0_{298}(j) \approx k_G [M_j/C_P(298)_j]^{1/3} n_j \quad (\mathrm{J\ K^{-1}\ mol^{-1}}) \qquad (17)$$

where k_G is a constant taken as 19.2 according to Ref. [16], M_j is molecular mass for the jth oxide and n_j is the number of atoms in the double oxide molecule.

(iii) The method of increments [17]

$$S^0_{298}(j) \approx \Delta S_K n_K + \Delta S_A n_A \quad (\mathrm{J\ K^{-1}\ mol^{-1}}) \qquad (18)$$

where ΔS_K and ΔS_A are standard entropies of the cation and anion respectively [17] (the values for Sr^{2+}, Bi^{3+} and O^{2-} are 43.0, 52.8 and 11.7 J K^{-1} mol^{-1}, respectively).

The results of calculations by Eqs. (16)–(18) agree. The average arithmetic value of $S^0_{298}(j)$ was taken as a reliable value (Table 3).

Table 3
Calculated standard entropies for 14 double oxides in the SrO–Bi_2O_3 system

Oxide	S^0_{298}/J mol^{-1} K^{-1} calculated by			$\bar{S}^0_{298}$/J mol^{-1} K^{-1} taken as reliable
	Eq. (16)	Eq. (17)	Eq. (18)	
$Sr_6Bi_2O_9$	482.230	461.780	468.900	471.0
$Sr_3Bi_2O_6$	316.00	309.810	304.800	310.2
$Sr_2Bi_2O_5$	260.580	258.930	250.100	256.5
$Sr_{18}Bi_{22}O_{51}$	2644.740	2644.080	2532.300	2607.0
$Sr_6Bi_{14}O_{27}$	1380.770	1403.290	1313.100	1365.7
$SrBi_4O_7$	354.930	364.190	336.100	351.7
$Sr_2Bi_6O_{11}$	560.095	572.030	531.500	554.5
$SrBi_2O_4$	205.169	207.800	195.400	202.8
$Sr_8Bi_{10}O_{23}$	1192.080	1192.570	1141.100	1175.3
$Sr_8Bi_2O_{11}$	593.050	562.820	578.300	578.1
$Sr_5Bi_6O_{14}$	704.400	700.200	695.600	700.0
$Sr_6Bi_2O_{11}$	482.230	461.78	468.900	471.0
$Sr_6Bi_4O_{15}$	632.000	619.620	609.600	620.4
$Sr_{24}Bi_{14}O_{52}$	2378.187	2321.000	2297.700	2332.3

2.3. Heat capacity

The temperature dependence of the heat capacities of the double oxides in the form

$$C_p(j) = a + b \times 10^3 T - c \times 10^5 T^{-2} \quad (\mathrm{J\,K^{-1}\,mol^{-1}}) \tag{19}$$

in the interval from 298 K to the temperature of the phase transformation was calculated in two ways:

(i) The additivity method of Neimann and Kopp

$$C_p(T)_j = \sum n_i C_p(T)_i \quad (\mathrm{J\,K^{-1}\,mol^{-1}}) \tag{20}$$

where $C_p(T)_i$ is the temperature dependence of the heat capacity of the ith simple oxide, and n_i is the number of moles of the ith simple oxide in the complex one.

(ii) The method described in Ref. [18]

The coefficients a, b and c calculated using both the above-mentioned ways agree. The mean arithmetic values $\bar{a}$, $\bar{b}$, and $\bar{c}$ are taken as reliable and are listed in Table 4.

The heat capacities of the double oxides at $T > T$ (phase transformation) were considered constant and were calculated by the equation [19]

$$C_p(j) \text{ at } T > T_{\mathrm{ph.tr}} \approx C_p(j)_{T_{\mathrm{ph.tr}}} + 0.25\Delta S_{\mathrm{ph.tr}} \quad (\mathrm{J\,K^{-1}\,mol^{-1}}) \tag{21}$$

2.4. Enthalpy increments H^0_{298}–H^0_0, T and ΔH of the phase transformations

The enthalpy increments have been calculated by the empirical dependence [20]

$$(H^0_{298}-H^0_0) \approx 216\,\bar{S}^0_{298}(j)\exp[-\bar{S}^0_{298}(j)/17] \quad (\mathrm{cal\,(g\,atom)^{-1}}) \tag{22}$$

Table 4
Calculated coefficients in the equation $C_p = a + b \times 10^{-3} T - c \times 10^5 T^{-2}$ in J mol^{-1} K^{-1} for 14 double oxides in the SrO–Bi_2O_3 system

Oxide	Calculated by Eq. (20)			Calculated according to Ref. [18]			Taken as reliable data		
	a	*b*	*c*	*a*	*b*	*c*	*a*	*b*	*c*
$Sr_6Bi_2O_9$	407.8	65.1	38.9	391.0	71.6	25.0	399.4	68.3	32.0
$Sr_3Bi_2O_6$	255.6	49.3	19.4	253.0	44.4	17.9	254.4	46.8	18.6
$Sr_2Bi_2O_5$	204.9	44.0	13.0	207.0	35.5	15.7	206.0	39.8	14.3
$Sr_{18}Bi_{22}O_{51}$	2051.2	462.9	116.7	2093.1	359.2	162.6	2072.1	411.0	139.7
$Sr_6Bi_{14}O_{27}$	1028.6	256.8	38.9	1081.0	177.3	89.8	1054.8	221.5	64.4
$SrBi_4O_7$	257.6	72.2	6.5	276.0	45.2	24.3	266.8	58.7	15.4
$Sr_2Bi_6O_{11}$	411.8	110.9	13.0	437.0	70.2	37.0	424.4	90.5	25.0
$SrBi_2O_4$	150.6	38.7	6.5	161.0	27.0	13.3	157.6	32.9	9.9
$Sr_8Bi_{10}O_{23}$	923.2	209.4	51.9	443.0	161.8	73.5	933.1	185.6	62.7
$Sr_8Bi_2O_{11}$	509.3	75.6	51.9	483.0	90.2	30.0	496.0	82.9	40.9
$Sr_5Bi_6O_{14}$	556.7	126.7	32.4	575.0	98.4	44.5	565.9	112.6	38.4
$Sr_6Bi_2O_{11}$	407.8	65.1	38.9	391.0	71.6	25.0	399.4	58.3	32.0
$Sr_6Bi_4O_{15}$	511.3	98.5	38.9	506.0	88.7	35.8	508.7	93.6	37.4
$Sr_{24}Bi_{14}O_{52}$	1940.4	360.7	155.6	1907.0	334.8	131.5	1925.4	347.8	143.5

where

$$\delta^0_{298}(j) = S^0_{298}(j)/n_j \quad (\mathrm{cal\ K^{-1}\ (g\ atom)^{-1}})$$

For some oxides, the temperature and types of phase transformation are known (Table 1). It can be from Table 1 that data from different investigators are not always in agreement. For $Sr_2Bi_2O_9$, $Sr_3Bi_2O_6$, $Sr_2Bi_2O_5$ and $SrBi_2O_4$, the data [7] are taken as being reliable. According to Ref. [5], $Sr_5Bi_6O_{14}$ melts at 1213 K without decomposition. For estimation of $T_{\mathrm{ph.tr}}$ of complex compounds in Ref. [10], an empirical dependence was assumed

$$T_{\mathrm{ph.tr}} \approx \bar{K} \sum x(i)\, T_{\mathrm{melt}}(i) \tag{23}$$

where $\bar{K}$ is an empirical correlating coefficient for a group of related substances and similar types of phase transformation, $x(i)$ is the molar fraction of the ith simple oxide in a complex compound, and $T_{\mathrm{melt}}(i)$ is the melting/decomposition temperature of the ith simple oxide.

For an analysis of $T_{\mathrm{ph.tr}}$ of complex oxides in the Y–Ba–Cu–O system [11], it was found that for various types of phase transformation, the $\bar{K}$ values can be represented as

$$\bar{K}_{\mathrm{CM}} = 0.94 \pm 0.03, \quad \bar{K}_{\mathrm{IM}} = 0.6973 \pm 0.006 \quad \text{and} \quad \bar{K}_{\mathrm{DCS}} = 0.582 \pm 0.05 \tag{24}$$

where CM, IM and DCS indicate congruent and incongruent melting, and decomposition in the crystalline state respectively.

Results of the calculations of $T_{\mathrm{ph.tr}}$ with the use of Eq. (23) and $\bar{K}_i$ values according to Eq. (24) are given in Table 5. For $Sr_6Bi_2O_9$, $Sr_3Bi_2O_6$, $Sr_2Bi_2O_5$ and $SrBi_2O_4$ the calculated and experimental data agrees with the mean deviation equal to +14.5%. The supposition about the CM-type of transformation for $Sr_5Bi_6O_{14}$ give the deviation equal to +62.6%; the supposition about the IM-type gives +20%. These results

Table 5
Temperatures and types of phase transformations for some double oxides in the $SrO–Bi_2O_3$ system

Oxide	$T_{\mathrm{ph.tr}}/\mathrm{K}$ and type of phase transform. by experiment	$T_{\mathrm{ph.tr}}/\mathrm{K}$ calculated with the use of Eqs. (23) and (24)	$\delta/\%$ difference between experimental and calculated data	$T_{\mathrm{ph.tr}}/\mathrm{K}$ calculated with the use of Eqs. (23) and (25)	$\delta/\%$ difference between experimental and calculated data
$Sr_6Bi_6O_9$	1238, DCS[a] [7]	1439, DCS	+ 16.2	1304, DCS	+ 5.3
$Sr_3Bi_2O_6$	1483, IM[a] [7]	1603, IM	+ 8.1	1439, IM	– 3,0
$Sr_2Bi_2O_5$	1213, IM [7]	1510, IM	+ 24.5	1343, IM	+ 10.7
$SrBi_2O_4$	1213, IM [7]	1322 IM	+ 9.0	1151, IM	– 5.1
$Sr_5Bi_6O_{14}$	1213, CM[a] [5]	(1972, CM)	(+ 62.6)	1295, IM	– 6.8
		1463, IM	+ 20.6		
			$\delta = +15.7$		$\delta = \pm 6.2$

[a] DCS, IM and CM indicate decomposition in the crystalline state, and incongruent and congruent melting, respectively.

give an average deviation, between calculated and experimental data, equal to +15.7% for 5 double oxides.

We made the corresponding correction for $\bar{K}_i$ values in the Eq. (23) and took the following revised values:

$$\bar{K}_{CM} \approx 0.79242, \quad \bar{K}_{IM} \approx 0.58782 \quad \text{and} \quad \bar{K}_{DCS} \approx 0.49063 \tag{25}$$

As can be seen from Table 5, application of the K coefficients in Eq. (23) gives an average deviation between the calculated and experimental data of ± 6.2%. Assuming that all the double oxides, besides those presented in Table 5, have a similar type of phase transformation (DCS), $T_{ph.tr.}$ can be calculated using Eq. (23) and $K_{DCS} \approx 0.49063$. After additional study of the phase diagram for $SrO–Bi_2O_3$, the types and temperatures of the phase transformations can be corrected.

Estimation of $\Delta H_{ph.tr.}$ values were carried out from the known dependence

$$\Delta H_{ph.tr}(j) = \Delta S_{ph.tr}(j)\, T_{ph.tr.}(j) \tag{26}$$

where the entropy change was calculated from the dependence [10]

$$\Delta S_{ph.tr}(j) \approx \sum n_i \Delta S_{ph.tr}(i) \tag{27}$$

where n_i is the number of moles of simple oxide in a complex one, and $\Delta S_{ph.tr}(i)$ is the entropy change during melting/decomposition of a simple oxide.

The T and ΔH phase transformation data for the simple oxides were taken from Ref. [9].

3. Discussion

The properties of 14 double oxides in the $SrO–Bi_2O_3$ system are collected in Table 6. The reliabilities of the different properties are not identical. The S^0_{298}, $H^0_{298}–H^0_0$ and $C_p(T)$ values for all the substances are estimated correctly enough. The SEF values were determined on the basis of experimental data [3] only, and in the future, SEF values can be corrected. The information on T and ΔH for phase transformations for the majority of the double oxides and also the C_p data at $T > T_{ph.tr}$ were deduced by empirical approximations and various suppositions. These data must be checked by experimental investigations.

The $\Delta H_R(j)$ values in Ref. [3] are equal to the $H^0_{at}(f)_j$ values used in this article. The revision of $\Delta H_R(j)$ data from Ref. [3] using the LAR [13] shows (see Fig. 1 and Table 2) that for 5 phases the $\Delta H_R(j)$ data obey the LAR with a mean deviation of ± 12.3%. But the ΔH_R for the composition "$Sr_{0.75}Bi_{0.25}$" [3] (or by our interpretation the $H^0_{at}(f)$ for phase $Sr_6Bi_2O_9$) does not agree with the LAR. The difference, however, is considerable: $\Delta H_R = -31.8$ kJ (g atom)$^{-1}$ [3] and $H^0_{at}(f) = -5.067$ kJ (g atom)$^{-1}$ according to the LAR (see points 2 and 2′ on Fig. 1). A possible explanation is the following. According to Refs. [1–6], in the $SrO–Bi_2O_3$ system $Sr_6Bi_2O_9$ (stoichiometric double oxide) and $Sr_6Bi_2O_{11}$ (double oxide with the surplus oxygen) can exist. If in Ref. [3] the composition "$Sr_{0.75}Bi_{0.25}$" means the phase $Sr_6Bi_2O_{11}$, then according to reactions (1) and (2)

Table 6
Thermochemical properties taken as reliable for 14 double oxides in the SrO–Bi_2O_3 system

Oxide	ΔH^0_{298}/ kJ mol^{-1}	S^0_{298}/ J mol^{-1} K^{-1}	H^0_{298}-H^0_0/ J mol^{-1}	$T_{ph.tr}$/ K	$\Delta H_{ph.tr}$/ kJ mol^{-1}	$c_p = a + b \times 10^{-3} T - c \times 10^5 T^{-2}$/ J mol^{-1} K^{-1}			$c_p$at $T > T_{ph.tr}$/ J mol^{-1} K^{-1}
						a	*b*	*c*	
$Sr_6Bi_2O_9$	−4207.4	471.0	68900	1238	261.7	399.4	68.3	32.0	534.7
$Sr_3Bi_2O_6$	−2443.4	310.2	45065	1483	199.9	254.4	46.8	18.6	356.6
$Sr_2Bi_2O_5$	−1860.3	265.5	37110	1213	132.5	206.0	39.8	14.3	280.6
$Sr_{18}Bi_{22}O_{51}$	−17928.9	2607.0	376330	1076	1099.5	2072.1	411.0	139.7	2777.0
$Sr_6Bi_{14}O_{27}$	−7927.6	1365.7	196020	922	516.7	1054.8	221.5	64.4	1392.0
$SrBi_4O_7$	−1803.5	351.7	50310	800	113.5	266.8	58.7	15.4	346.8
$Sr_2Bi_6O_{11}$	−3029.6	554.5	79450	864	194.9	424.4	90.5	25.0	555.7
$SrBi_2O_4$	−1224.2	202.8	29140	1213	101.5	157.6	32.9	9.9	217.8
$Sr_8Bi_{10}O_{23}$	−8033.1	1175.3	169620	1070	529.8	933.1	185.6	62.7	1250.0
$Sr_8Bi_2O_{11}$	−5387.5	578.1	84770	1335	350.3	496.2	82.9	40.9	670.2
$Sr_5Bi_6O_{14}$	−4902.7	700.0	101975	1213	366.6	565.9	112.6	38.4	775.4
$Sr_6Bi_2O_{11}$	−4391.4	471.0	68900	1238	261.7	399.4	68.3	32.0	534.7
$Sr_6Bi_4O_{15}$	−5162.7	620.4	90130	1200	323.4	508.7	93.6	37.4	685.8
$Sr_{24}Bi_{14}O_{52}$	−19201.2	2332.3	339290	1224	1248.4	1925.4	347.8	143.5	2594.0

and our suppositions

$$\begin{aligned}\Delta H_R(\mathrm{Sr_6Bi_2O_{11}}) &= H^0_{at}(f)(\mathrm{Sr_6Bi_2O_9}) = 1\,\Delta H_{02}/n_j \\ &= -5.067 + (184/19) = -14.751 \quad (\mathrm{kJ\,(g\,atom)^{-1}}) \qquad (28)\end{aligned}$$

As can be seen, the absolute value of ΔH_R in this case is also 2.16 times less than ΔH_R given in Ref. [3] (see p. 2″ and 2 in Fig. 1). It is also interesting that in the other investigation [3] of 13 complex oxides containing Sr and Bi, the $\Delta H_R(j)$ values were not lower than -13 kJ (g atom)$^{-1}$. Therefore, we can conclude that the ΔH_R value of -31.8 kJ (g atom)$^{-1}$ for the composition "$\mathrm{Sr_{0.75}Bi_{0.25}}$" [3] is incorrect.

On the basis of the analysis of known $T_{\mathrm{ph.tr}}$ together with the use of the empirical dependences (23)–(25), we conclude that for $\mathrm{Sr_5Bi_6O_{14}}$ the type of phase transformation is incongruent melting, although congruent melting was reported in Ref. [5].

Assuming that for the 11 stoichiometric double oxides, the $\Delta H^0_{298}(\mathrm{ox})_j$ values are reliable, we can proceed to revise the numerical coefficient in Eq. (10) (Table 7). The initial data are given in columns 2 and 3. The average difference between those calculated by Eq. (10) and those taken as reliable $\Delta H^0_{298}(\mathrm{ox})_j$ is 119.5%, i.e. all deviations have the same sign and show that the use of Eq. (10) gives a more negative $\Delta H^0_{298}(\mathrm{ox})_j$. To estimate a new numerical coefficients (K'), we have to find how much the result differs on average ($\Sigma''/\Sigma' = -4929/-2702.16 = 1.8241$), changing $K = -29.274$ kJ mol^{-1} ($K' = K/1.8241$) to -16.0485 kJ mol^{-1}. The average difference of the $\Delta H^0_{298}(\mathrm{ox})_j$ data calculated with the help of K' and taken as reliable is equal

Table 7
Data for correction of the numerical coefficient K in the equation $H^0_{298}(\mathrm{ox})_j \approx K m_0(j)$ [14]

Oxide	ΔH^0_{298}(ox)/kJ mol^{-1}		δ/%difference between calculated and reliable data	ΔH^0_{298}(ox)/ kJ mol^{-1} by corrected Eq. (29)	δ/% difference between corrected and reliable data
	By Eq. (10)	Taken as reliable			
$\mathrm{Sr_6Bi_2O_9}$	−263.5	−86.14	−205.9	−144.4	−67.7
$\mathrm{Sr_3Bi_2O_6}$	−175.6	−97.50	−80.1	−95.3	+1.2
$\mathrm{Sr_2Bi_2O_5}$	−146.4	−106.20	−37.8	−80.2	+24.4
$\mathrm{Sr_{18}Bi_{22}O_{51}}$	−1494.0	−1001.00	−49.2	−818.2	+18.2
$\mathrm{Sr_6Bi_{14}O_{27}}$	−790.4	−383.28	−106.2	−433.3	−13.0
$\mathrm{SrBi_4O_7}$	−204.9	−70.68	−189.9	−112.3	−58.9
$\mathrm{Sr_2Bi_6O_{11}}$	−322.0	−134.45	−139.5	−176.5	−31.3
$\mathrm{SrBi_2O_4}$	−117.1	−61.92	−89.1	−64.2	−3.7
$\mathrm{Sr_{18}Bi_{10}O_{23}}$	−673.3	−446.16	−50.9	−369.1	+17.3
$\mathrm{Sr_8Bi_2O_{11}}$	−322.0	−82.63	−289.7	−176.5	−113.6
$\mathrm{Sr_5Bi_6O_{14}}$	−409.8	−232.20	−76.5	−224.7	−3.2
$\sum'' = -4929.0$,		$\sum' = -2702.16$,	$\delta = +119.5$		$\delta = \pm 32.0$

Table 8
The coefficients of temperature dependences of the reduced Gibbs energy (22) in J k^{-1} mol^{-1} for some phases in the SrO–Bi_2O_3 system[a]

Oxide	Temperature interval/K	φ_1	φ_2	φ_3	φ_4	φ_5
$Sr_6Bi_2O_9$	298–1238	1436.42	399.4	−0.016	6.38922	341.5
	> 1238	1880.76	534.701	0	8.52311	0
$Sr_3Bi_2O_6$	298–1483	925.152	254.4	−0.0093	3.90659	234.0
	> 1483	1222.62	356.6	0	6.19892	0
$Sr_2Bi_2O_5$	298–1213	656.574	206.0	−0.00715	4.67487	1990
	> 1213	1331.84	280.6	0	−28.9243	0
$Sr_{18}Bi_{22}O_{51}$	298–1076	7613.57	2072.1	−0.06985	30.6285	2055
	> 1076	9950.24	2777.0	0	−28.565	0
$Sr_6Bi_{14}O_{27}$	298–922	3914.41	1054.8	−0.0322	14.9756	1107.5
	> 922	5149.45	1392.0	0	−15.7177	0
$SrBi_4O_7$	298–800	996.072	266.8	−0.0077	3.69706	293.5
	> 800	1308.17	346.8	0	−3.32385	0
$Sr_2Bi_6O_{11}$	298–864	1337.36	424.4	−0.0125	9.55944	4525.01
	> 864	2536.75	555.701	0	−32.6546	0
$SrBi_2O_4$	298–1213	583.51	157.6	−0.00495	2.26078	164.5
	> 1213	774.222	217.8	0	−3.08898	0
$Sr_8Bi_{10}O_{23}$	298–1070	3429.8	933.101	−0.03135	13.7725	928.001
	> 1070	4517.62	1250.0	0	−16.5099	0
$Sr_8Bi_2O_{11}$	298–1335	1777.44	496.201	−0.02045	8.05034	414.5
	> 1335	2328.03	670.201	0	−11.4444	0
$Sr_5Bi_6O_{14}$	298–1213	2067.07	565.908	−0.0192	8.45489	563.010
	> 1213	2739.63	775.401	0	−11.3932	0
$Sr_6Bi_2O_{11}$	298–1238	1436.42	339.4	−0.016	6.38922	341.5
	> 1238	1880.76	534.701	0	−8.52311	0
$Sr_6Bi_4O_{15}$	298–1200	1849.94	508.701	−0.00187	7.81691	468.001
	> 1200	2431.46	685.801	0	−10.322	0
$Sr_{24}Bi_{11}O_{52}$	298–1224	7148.46	1925.4	−0.07175	20.1768	1739.0
	> 1224	8306.17	2594.0	0	77.0078	0

[a] φ_6 and φ_7 are zero.

to ± 32.0%. Consequently, after revision

$$\Delta H^0_{298}(\mathrm{ox})_j \approx (-16.0485 \pm 5.145) m_0(j) \quad (\mathrm{kJ\ mol^{-1}}) \tag{29}$$

For further thermodynamic simulation [12] for all the double oxides in question, the temperature polynomial approximating the temperature dependences of the reduced Gibbs energy in the interval from 298 to 6000 K was calculated

$$\Phi^*(T)_j = \varphi_1 + \varphi_2 \ln x + \varphi_3 x^{-2} + \varphi_4 x^{-1} + \varphi_5 x + \varphi_6 x^2 + \varphi_7 x^3 (\mathrm{kJ\ K^{-1}\ mol^{-1}}) \tag{30}$$

where φ_i are numerical coefficients and $x = 10^{-4}\ T(\mathrm{K})$ (Table 8).

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