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Standard enthalpy of formation and heat capacity of compounds in the pseudo-binary Bi_2O_3–Fe_2O_3 system

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Abstract

Bismuth ferrites, $Bi_2Fe_4O_9$, $BiFeO_3$, and $Bi_{25}FeO_{39}$ have been prepared and characterized. The thermodynamic data such as standard molar enthalpies of formation $\Delta_f H^\circ_m$(298.15 K) and standard molar heat capacity ($C_p{}^\circ$) were obtained from the solution calorimetry and calvet calorimetric measurements. $\Delta_f H^\circ_m(298.15\,K)$ for $Bi_2Fe_4O_9$(s), $BiFeO_3$(s), and $Bi_{25}FeO_{39}$(s) were found to be (-2476.0 ± 4.3), (-768.4 ± 2.9) and (-7699.8 ± 17.3) kJ mol^{-1}, respectively. The dependence of molar heat capacity C°_p with temperature can be given as

$$C^\circ_p(\mathrm{Bi_2Fe_4O_9, s})\ (\mathrm{J\,K^{-1}\,mol^{-1}}) = 353.81 + 0.01774T - 1.63606 \times 10^5/T^2 \quad (313 < T/\mathrm{K} < 911)$$

$$C^\circ_p(\mathrm{BiFeO_3, s})\ (\mathrm{J\,K^{-1}\,mol^{-1}}) = 116.72 + 0.00968T - 1.9273 \times 10^5/T^2 \quad (313 < T/\mathrm{K} < 911)$$

and

$$C^\circ_p(\mathrm{Bi_{25}FeO_{39}, s})\ (\mathrm{J\,K^{-1}mol^{-1}}) = 1339.21 + 0.16550T - 28.3546 \times 10^5/T^2 \quad (324 < T/\mathrm{K} < 834).$$

The standard Gibbs energy of formation of the above compounds have been derived using the values of $\Delta_f H^\circ_m$ (298.15 K), C°_p and the estimated $\Delta_f S^\circ_m$ (298.15 K).

1. Introduction

The lead–bismuth eutectic alloy (Pb–55.2 wt% Bi), a potential target material for accelerator driven sub-critical reactor systems (ADS) is envisaged for the transmutation of radioactive wastes such as minor actinides and long-lived fission products [1–5]. The Pb–55.2 wt% Bi alloy has the required qualities of the target material such as: high atomic number, low melting point, low vapor pressure at working temperatures (≅950 °C) and low parasitic neutron absorption cross-section. However, it is known from the literature that at high temperatures there are corrosion problems of the steel based container material like T91steel (9Cr, 1Mo) in contact with the liquid alloy [6–9]. Besides the long contact period, the corrosion process depends upon chemical factors like oxygen content in the alloy, and nature of corrosion products formed at the solid–liquid interface. Though Pb and Bi is known to have less stable oxides, there can be the formation of ternary oxides particularly of Bi and Fe on the steel surface. Depending upon the oxygen content the steel containers can be oxidized to form different oxide layers that redistribute in the melt. For the long term behavior of the structural material containing the liquid bath, the thermodynamic knowledge of the multi-component Pb–Bi–Fe–O is needed. The corrosion tests in the condition reproducing those of the reactors have indicated the formation of products like Fe_3O_4, $Fe_{(1-x)}Cr_xFe_2O_4$, $Bi_{25}FeO_{39}$ [10]. Investigations in the Bi–Fe–O system concerning the physico-chemical characteristics of the pseudo-binary Bi_2O_3–Fe_2O_3 system have been done by several authors [9–11]. Maitre et al. have reported the modified version of the pseudo-binary

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Bi_2O_3–Fe_2O_3 system [12]. However, thermodynamic properties of these compounds are not available in the literature. In this paper, we report the standard enthalpy of formation and heat capacity of bismuth ferrites, $Bi_2Fe_4O_9$, $BiFeO_3$, and $Bi_{25}FeO_{39}$.

2. Experimental

2.1. Preparation

Bismuth ferrites were prepared from high purity Bi_2O_3 (99.99%) and Fe_2O_3 (Aldrich, purity 99.99%). For preparation of the compounds, $Bi_2Fe_4O_9$, $BiFeO_3$, and $Bi_{25}FeO_{39}$ thoroughly ground mixtures of Bi_2O_3 and Fe_2O_3 in appropriate molar proportions were pelletized and heated in air at 873, 1023 and 750 K, respectively for 100 h in a platinum boat with two intermittent grindings. No mass change due to vaporization loss was observed in these samples.

2.2. Characterization

The compounds formed were characterized by XRD technique in a Philips X-ray diffractrometer (PW-1729) using Cu Kα radiation. The composition of the single-phase compounds were established from the chemical analyses of the samples using atomic absorption spectroscopy (AAS) (Chemito 203) and differential pulsed polarographic (DPP) technique (Autolab PGSTAT-20, Metrohm VA663 Stand). DTA runs for the compounds were taken in a commercial TG-DTA apparatus (Setaram, 92-16.18) in argon atmosphere at a heating rate of 10 K min^{-1} to check their melting points.

2.3. Solution calorimetric measurements

The enthalpies of dissolution of $Bi_2Fe_4O_9$, $BiFeO_3$ and $Bi_{25}FeO_{39}$ were measured in an isoperibol solution calorimeter operated at 298 K. The construction and operation of the calorimeter are similar to the one described by Athavale et al. [13]. For each of these compounds the samples were weighed and introduced into a glass bulb, which were then thermally equilibrated in the calorimetric solution. The solvent used was 0.150 dm^3 of aqueous 11.92 mol dm^{-3} HCl. The glass bulb was broken to introduce the sample into the solution when a steady state thermal signal was obtained on the strip chart recorder. The energy equivalent of the calorimeter was determined before and after each measurement by electrical calibration. The enthalpies of dissolution of Bi_2O_3(s) and Fe_2O_3(s) were also measured in the same solvent. Using these experimental values and other auxiliary data from literature the enthalpies of formation of $Bi_2Fe_4O_9$, $BiFeO_3$ and $Bi_{25}FeO_{39}$ were determined.

2.4. Heat capacity measurements

The pellets of $Bi_2Fe_4O_9$(s), $BiFeO_3$(s) and $Bi_{25}FeO_{39}$(s) were annealed in air at 800 K for 50 h and stored in a desiccator for $H°(T)–H°$ (298.15 K) measurements. The Calvet calorimeter model HT-1000, was used for the measurements of enthalpy increments of the compounds and the drop technique of sample was adopted. The calorimeter has an isothermal alumina block which contains two identical one-end-closed alumina cells surrounded by a series of thermopiles. The sample, in the form of a pellet, maintained at 298 K in the sample holder, was dropped into the sample cell at the experimental temperature. The ranges of temperature used were 313–911 K for $Bi_2Fe_4O_9$ and 313–911 K for $BiFeO_3$ and 324–834 K for $Bi_{25}FeO_{39}$. The last compound has a reported melting point of 1065 K [12]. The temperature of the isothermal block of the calorimeter was measured using a Pt–Pt10% Rh thermocouple (±0.1 K). The heat flow between the isothermal block and either of the cells was recorded in the form of a millivolt signal of the thermo-emf. The details of the experimental measurements have been described elsewhere [14]. The heat calibration was carried out using a synthetic sapphire [NIST SRM-720].

3. Results

Fig. 1 gives the XRD patterns of the compounds $Bi_2Fe_4O_9$, $BiFeO_3$ and $Bi_{25}FeO_{39}$, which matched well with that reported data in JCPDS file Nos. 20-0836, 20-01690, and 46-0416, respectively. No lines due to the starting components Bi_2O_3 and Fe_2O_3 and impurity phases were found. The XRD patterns for $Bi_2Fe_4O_9$, $BiFeO_3$ and $Bi_{25}FeO_{39}$ could be indexed with orthorhombic, rhombohedral and cubic structures respectively. The cell parameters (in nm) were found to be $a = 0.7974(4)$, $b = 0.8437(6)$, $c = 0.5991(6)$ for $Bi_2Fe_4O_9$, $a = 0.5576(6)$, $\alpha = 89.47(2)$ for $BiFeO_3$, and $a = 1.0177(2)$ for $Bi_{25}FeO_{39}$ against the reported values ($a = 0.7965$, $b = 0.8444$, $c = 0.5994$), ($a = 0.5572$, $\alpha = 89.468$), and ($a = 1.018$) for the respective cases. The results of the chemical analysis of the ferrites

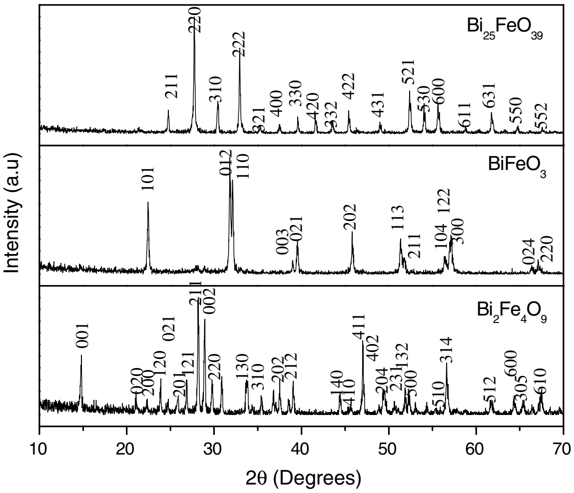

Fig. 1. XRD patterns of $Bi_2Fe_4O_9$, $BiFeO_3$ and $Bi_{25}FeO_{39}$ compounds.

Table 1
The molar enthalpies of dissolution of $Bi_2Fe_4O_9(s)$, $BiFeO_3(s)$, $Bi_{25}FeO_{39}(s)$, $Bi_2O_3(s)$ and $Fe_2O_3(s)$ in 0.150 dm^3 aqueous solution of 11.92 mol dm^{-3} HCl at $T = 298.15$ K; m denotes the mass of the sample dissolved; ΔH is the measured energy change per unit mass and $\Delta_{sol}H_m$ is the molar enthalpy of solution

Solute	m (solute) (gm)	ΔH (J/gm)	$\Delta_{sol}H_m$ (kJ mol^{-1})
$Bi_2Fe_4O_9(s)$ Mol. Mass = 785.35	0.1090	−678.67	−533.0
	0.1742	−678.67	−533.0
	0.0787	−675.59	−530.6
	0.1737	−676.69	−531.4
	0.1829	−678.32	−532.7
			Average: −532.1 ± 1.1
$BiFeO_3(s)$ Mol. Mass = 312.83	0.1609	−740.89	−231.8
	0.1365	−745.46	−233.2
	0.1192	−739.13	−231.2
	0.1142	−757.48	−237.0
			Average: −233.3 ± 2.6
$Bi_{25}FeO_{39}(s)$ Mol. Mass = 5904.31	0.0491	−894.80	−5283.2
	0.0497	−896.11	−5290.9
	0.0547	−895.62	−5288.0
	0.0527	−895.35	−5286.4
			Average: −5287.1 ± 3.2
$Bi_2O_3(s)$ Mol. Mass = 465.96	0.0678	−907.97	−423.1
	0.0607	−911.75	−424.8
	0.0662	−913.08	−425.5
	0.0685	−912.52	−425.2
			Average: −424.7 ± 1.1
$Fe_2O_3(s)$ Mol. Mass = 159.694	0.0241	−1144.05	−182.7
	0.0079	−1159.83	−185.2
	0.0354	−1155.57	−184.5
	0.0555	−1135.02	−181.3
			Average: −183.4 ± 1.8

show that the mass percentages of Bi and Fe in the compounds agree very well with those of the expected values.

The results of the enthalpies of dissolution of $Bi_2Fe_4O_9(s)$, $BiFeO_3(s)$, $Bi_{25}FeO_{39}(s)$, $Bi_2O_3(s)$ and $Fe_2O_3(s)$ are given in Table 1. The thermochemical cycles from which the standard molar enthalpies of formation of $Bi_2Fe_4O_9(s)$, $BiFeO_3(s)$ and $Bi_{25}FeO_{39}(s)$ have been derived are given in Table 2. The experimentally measured values using the above cycles were combined with other auxiliary data such as the standard enthalpies of formation of $Bi_2O_3(s)$ and $Fe_2O_3(s)$ from the literature [16] to derive the standard molar enthalpies of formation of $Bi_2Fe_4O_9(s)$, $BiFeO_3(s)$ and $Bi_{25}FeO_{39}(s)$ at 298.15 K. The values are (-2476.0 ± 4.3) kJ mol^{-1} and (-768.4 ± 2.9) kJ mol^{-1} and (-7699.0 ± 17.3) kJ mol^{-1} for $Bi_2Fe_4O_9(s)$, $BiFeO_3(s)$ and $Bi_{25}FeO_{39}(s)$, respectively.

The molar heats of dissolution for $Bi_2Fe_4O_9(s)$, $BiFeO_3(s)$ and $Bi_{25}FeO_{39}(s)$ in the aqueous HCl when plotted against their respective molar concentration show that there is no significant dilution effect and the experiments were carried out effectively under infinite dilution conditions in each case. So in each case the average of four values were taken.

4. Enthalpy increment

The enthalpy increment $H°(T)–H°$ (298.15 K) values for $Bi_2Fe_4O_9(s)$, $BiFeO_3(s)$ and $Bi_{25}FeO_{39}(s)$ obtained at different temperatures are given in Tables 3–5, respectively. The reproducibility of the data obtained by dropping the samples at a fixed temperature several times were found to be within ±0.05%. The enthalpy increment values for these compounds were plotted against temperature. Fig. 2 gives the $H_T–H_{298}$ plots as a function of temperature for $Bi_2Fe_4O_9(s)$, $BiFeO_3(s)$ and $Bi_{25}FeO_{39}(s)$ compounds. The best least-square fitted line passing through the maximum number of points was extrapolated to 298.15 K. Observed enthalpy increment data given in Tables 3–5 were fitted using Shomate's method [15] with the boundary conditions: $H°(T)–H°$ (298.15 K) = 0 at 298.15 K within experimental uncertainty. The expressions $H°(T)–H°$ (298.15 K)

Table 2
Reaction scheme for the standard molar enthalpy of formation in 0.150 dm^3 of 11.92 mol dm^{-3} HCl for $Bi_2Fe_4O_9(s)$, $\Delta_f H°_{298.15} = -\Delta H_1 + \Delta H_4 + 2\Delta H_5 + \Delta H_6 + 2\Delta H_7$ $BiFeO_3(s)$, $\Delta_f H°_{298.15} = 0.5[-2\Delta H_2 + \Delta H_4 + \Delta H_5 + \Delta H_6 + \Delta H_7]$ $Bi_{25}FeO_{39}(s)$, $\Delta_f H°_{298.15} = -\Delta H_3 + 25/2\Delta H_4 + 1/2\Delta H_5 + 25/2\Delta H_6 + 1/2\Delta H_7$

Reaction	ΔH_i	ΔH_m/kJ mol^{-1} (298.15 K)	References
$Bi_2Fe_4O_9(s) + 18\ HCl(sln) = (2\ BiCl_3 + 4\ FeCl_3 + 9\ H_2O)(sln)$	ΔH_1	−532.1 ± 1.1	This work
$BiFeO_3(s) + 6\ HCl(sln) = (BiCl_3 + FeCl_3 + 3H_2O)(sln)$	ΔH_2	−233.3 ± 2.6	This work
$Bi_{25}FeO_{39}(s) + 78\ HCl(sln) = (25\ BiCl_3 + FeCl_3 + 39H_2O)(sln)$	ΔH_3	−5287.1 ± 3.2	This work
$Bi_2O_3(s) + 6\ HCl(sln) = (2\ BiCl_3 + 3H_2O)(sln)$	ΔH_4	−424.7 ± 1.1	This work
$Fe_2O_3(s) + 6HCl(sln) = 2FeCl_{3(s)} + 3H_2O(sln)$	ΔH_5	−183.4 ± 1.8	This work
$2Bi(s) + 3/2O_2(g) = Bi_2O_3(s)$	ΔH_6	−574.0 ± 0.8	[16]
$2Fe(s) + 3/2\ O_2(g) = Fe_2O_3(s)$	ΔH_7	−821.3 ± 0.8	[16]
$2Bi(s) + 4Fe(s) + 9/2O_2(g) = Bi_2Fe_4O_9(s)$	$\Delta_f H_{298.15}$	−2476.0 ± 4.3	This work
$Bi(s) + Fe(s) + 3/2O_2(g) = BiFeO_3(s)$	$\Delta_f H_{298.15}$	−768.4 ± 2.9	This work
$25Bi(s) + Fe(s) + 39/2O_2(g) = Bi_{25}FeO_{39}(s)$	$\Delta_f H_{298.15}$	−7699.8 ± 17.3	This work

Table 3
Enthalpy increment data for $Bi_2Fe_4O_9$(s)

Temperature (K)	Mass (mg)	$H_T - H_{298}$ observed (Ho) (J/mol)	$H_T - H_{298}$ fitted (Hf) (J/mol)	% error (Hf − Ho)/Hf × 100
313.8	87.6	1579	1842	14.32
323	90.8	4963	5135	3.33
349	138.9	13990	14450	3.15
374	72.5	22870	23430	2.37
400	58.0	32180	32770	1.82
426	118.6	41230	42140	2.15
453	82.8	53460	51880	−3.04
476	145.2	60020	60190	0.27
502	78.3	70290	69600	−1.00
528	67.3	78930	79020	0.11
553	99.4	83500	88090	5.20
579	96.6	93560	97530	4.07
604.5	147.8	108100	106800	−1.22
630	69.8	116200	116100	−0.12
655.5	124.4	130400	125400	−4.00
681	124.6	136600	134700	−1.37
706.5	100.6	142900	144000	0.81
732	97.9	151700	153400	1.08
757	119.4	165600	162600	−1.86
783	82.5	173200	172100	−0.67
809	97.7	180700	181700	0.53
834	101.3	189800	190900	0.54
861	86.1	202600	200800	−0.87
885	76.9	209800	209700	−0.07
911	106.4	218200	219300	0.51

Table 4
Enthalpy increment data for $BiFeO_3$(s)

Temperature (K)	Mass (mg)	$H_T - H_{298}$ observed (Ho) (J/mol)	$H_T - H_{298}$ fitted (Hf) (J/mol)	% error (Hf − Ho)/Hf × 100
313.3	25.6	1329.5	1334.9	0.40
324	25.6	2571.5	2596.4	0.96
334	45.3	3800.8	3777.8	−0.61
344.1	39.4	5030.3	4972.8	−1.15
354.2	33.8	6266.0	6169.9	−1.56
400.2	67.0	11403	11644	2.07
425.9	94.9	20204	20797	2.68
502.1	120.7	24003	23885	−0.49
527.9	129.4	26750	27007	0.95
556.4	82.0	30692	30464	−0.75
578.9	143.1	33739	33200	−1.62
604.5	41.0	36069	36321	0.69
629.9	68.8	39273	39425	0.38
655.6	87.0	43440	42572	−2.04
680.9	85.5	45551	45678	0.28
706.6	180.3	48770	48840	0.14
732.2	49.0	51417	51997	1.11
757.6	56.7	55027	55136	0.20
783.5	70.4	58906	58344	−0.96
808.9	98.7	61721	61496	−0.37
834.6	49.5	64193	64693	0.77
859.9	31.2	67731	67847	0.17
885.5	79.4	71122	71045	−0.11
910.9	75.6	74479	74224	−0.34

Table 5
Enthalpy increment data for $Bi_{25}FeO_{39}$(s)

Temperature (K)	Mass (mg)	$H_T - H_{298}$ observed (Ho) (J/mol)	$H_T - H_{298}$ fitted (Hf) (J/mol)	% error (Hf − Ho)/Hf × 100
324	40.8	34894	32840	−6.25
334	93.8	46525	46514	−0.02
344.5	67.9	62408	60907	−2.46
354.5	93.0	76165	74645	−2.03
364.5	80.0	89863	88413	−1.63
374.5	70.5	1022000	1022000	0.01
400	64.4	1358500	1375100	1.20
425.5	34.9	1705700	1729700	1.38
449	109.6	2030400	2058000	1.33
475	47.3	2355800	2422600	2.75
502	65.2	2773200	2800028	1.05
527	54.1	3144000	3163300	0.60
553	41.3	3534910	3532200	−0.07
578.5	49.4	3895070	3888200	−0.17
604.5	40.6	4267000	4259800	−0.17
630	29.8	4668500	4625400	−0.93
655.5	47.1	5016800	4992300	−0.49
681	46.4	5370500	5360400	−0.18
706.5	23.5	5789700	5729600	−1.04
732	28.0	6168200	6100100	−1.11
758	27.7	6507100	6479000	−0.43
783	23.2	6849500	6844500	−0.07
809	35.0	7202000	7225800	0.32
834.5	28.7	7487200	7600900	1.50

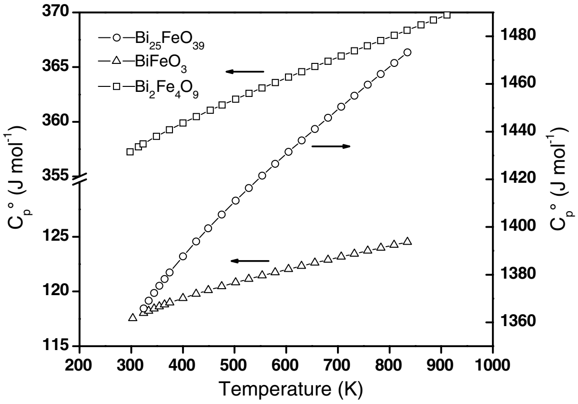

Fig. 2. Plot of C_p vs. temperature for $Bi_2Fe_4O_9$(s), $BiFeO_3$(s) and $Bi_{25}FeO_{39}$(s) compounds.

for $Bi_2Fe_4O_9$(s), $BiFeO_3$(s) and $Bi_{25}FeO_{39}$(s) can be expressed by the relations: $353.81T + 8.87\times10^{-3}T^2 + 1.63606\times10^5/T - 110578$ J mol^{-1} (298 < T/K < 911), $116.72T + 4.840\times10^{-3}T^2 + 1.9273\times10^5/T - 36323.7$ J mol^{-1} (313 < T/K < 911) and $1339.21\ T + 82.75\times10^{-3}T^2 + 28.35464\times10^5/T - 418502$ J mol^{-1} (324 < T/K < 834), respectively. The corresponding C_p° values from these plots were found to be

$$C_p^\circ(\mathrm{Bi_2Fe_4O_9, s})\ (\mathrm{J\ K^{-1}\ mol^{-1}})$$

$$= 353.81 + 0.01774T - 1.63606\times10^5/T^2$$

$$(313 < T/\mathrm{K} < 911),$$

$$C^\circ_{p\,298.15} = 357.3\ \mathrm{J\ K^{-1}\ mol^{-1}} \cong 23.8\ \mathrm{J/K\ g\ at},$$

$$C_p^\circ(\mathrm{BiFeO_3, s})\ (\mathrm{J\ K^{-1}\ mol^{-1}}) = 116.72 + 0.00968T - 1.9273 \times 10^5/T^2 \quad (313 < T/\mathrm{K} < 911),$$

$$C^\circ_{p\,298.15} = 117.4\mathrm{J\ K^{-1}\ mol^{-1}} \cong 23.5\ \mathrm{J/K\ g\ at},$$

and

$$C_p^\circ(\mathrm{Bi_{25}FeO_{39}, s})\ (\mathrm{J\ K^{-1}\ mol^{-1}}) = 1339.21 + 0.16550.T - 28.3546 \times 10^5/T^2 \quad (324 < T/\mathrm{K} < 834)$$

$$C^\circ_{p\,298.15} = 1356.3\ \mathrm{J\ K^{-1}\ mol^{-1}} \cong 20.9\ \mathrm{J/K\ g\ at}$$

The C_p° values for the compounds $Bi_2Fe_4O_9$(s), $BiFeO_3$(s) and $Bi_{25}FeO_{39(s)}$ were also estimated from the heat capacity values of Bi_2O_3(s) and Fe_2O_3(s) using Neumann–Kopp rule and compared with the experimental data.

5. Standard Gibbs energy of formation of $Bi_2Fe_4O_9$(s), $BiFeO_3$(s) and $Bi_{25}FeO_{39}$(s)

Gibbs energy of formation of the $Bi_2Fe_4O_9$(s), $BiFeO_3$(s) and $Bi_{25}FeO_{39}$(s) were derived using the standard enthalpies of formation data of the compounds together with their respective standard heat capacity change (ΔC_p°) and estimated entropy change ($\Delta S^\circ_{298.15}$) for the formation reaction using the relation

$$\Delta_f G^0_T = \Delta_f H^0_{298.15} + \int_{298.15}^{T} \Delta_f C_p^0 \cdot \mathrm{d}T - T \cdot \left[\Delta_f S^0_{298.15} + \int_{298.15}^{T} \frac{\Delta_f C_p^0}{T}\mathrm{d}T\right].$$

The standard molar heat capacity ($\Delta_f C^\circ_{p\,298.15}$) and entropy of formation ($\Delta_f S^\circ_{298.15}$) for the $Bi_2Fe_4O_9$(s), $BiFeO_3$(s) and $Bi_{25}FeO_{39}$(s) were estimated by adding molar $\Delta_f C^\circ_{p\,298.15}$ and $\Delta_f S^\circ_{298.15}$ values of the component oxides Bi_2O_3(s) and Fe_2O_3(s) [16] in the stoichiometric ratio of the respective compounds with the assumption that there is negligible change in the molar properties of the formation reactions. $\Delta_f S^\circ_{298.15}$ for the $Bi_2Fe_4O_9$(s), $BiFeO_3$(s) and $Bi_{25}FeO_{39}$(s) estimated in this way are −782.22, −262.95, −3498.02 $\mathrm{J\ K^{-1}\ mol^{-1}}$, respectively. Making use of the measured quantities such as $\Delta_f H^\circ_{298.15}$ and C_p° of the compounds $Bi_2Fe_4O_9$(s), $BiFeO_3$(s) and $Bi_{25}FeO_{39}$(s), and the estimated values of $\Delta_f C^\circ_{p\,298.15}$, $\Delta_f S^\circ_{298.15}$, the standard Gibbs energy of formation of these compounds are derived to be $-2459.1 + 0.757\mathrm{T}$, $-773.3 + 0.269\mathrm{T}$ and $-7355.2 + 2.669\mathrm{T}$ $\mathrm{k\ J\ mol^{-1}}$, respectively in the temperature range of 298.15–911 K.

6. Conclusion

The standard enthalpies of formation of $Bi_2Fe_4O_9$(s), $BiFeO_3$(s) and Bi25FeO_{39}(s) at 298.15 K are found to be $-(2476.0 \pm 4.3)\ \mathrm{kJ\ mol^{-1}}$ and $-(768.4 \pm 2.9)\ \mathrm{kJ\ mol^{-1}}$ and $-(7699.8 \pm 17.3)\ \mathrm{kJ\ mol^{-1}}$, respectively. The heat capacities of $Bi_2Fe_4O_9$(s), $BiFeO_3$(s) and $Bi_{25}FeO_{39}$(s) derived from the measured H_T–$H_{298.15}$ values were found to be $353.81 + 0.01774T - 1.63606 \times 10^5/T^2$ $(298 < T/\mathrm{K} < 911)\ \mathrm{J\ K^{-1}\ mol^{-1}}$, $116.72 + 0.00968T - 1.9273 \times 10^5/T^2$ $(313 < T/\mathrm{K} < 911)\ \mathrm{J\ K^{-1}\ mol^{-1}}$ and $1339.21 + 0.16550T - 28.3546 \times 10^5/T^2$ $(324 < T/\mathrm{K} < 834)\ \mathrm{J\ K^{-1}\ mol^{-1}}$, respectively. The standard Gibbs energy of formation of the compounds obtained from the enthalpy of formation data, heat capacity data is the first report of the data on these three compounds.

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