Journal of Nuclear Materials 404 (2010) 9–18

Contents lists available at ScienceDirect

Journal of Nuclear Materials

journal homepage: www.elsevier.com/locate/jnucmat

Calorimetric investigations on stoichiometric barium and uranium oxides

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ARTICLE INFO

Article history:
Received 5 February 2010
Accepted 11 June 2010

ABSTRACT

Heat capacities and enthalpy increments of barium uranates: $BaU_2O_7(s)$, $Ba_2U_3O_{11}(s)$, $Ba_{2.875}UO_{5.875}(s)$ and $Ba_3UO_6(s)$ were measured using a differential scanning calorimeter and a high-temperature Calvet calorimeter. The heat capacities and enthalpy increments were measured in the temperature range 126–304 K and 299–1011 K, respectively. A set of self consistent thermodynamic functions such as entropy, Gibbs energy function, heat capacity and Gibbs energy and enthalpy of formation values for $BaU_2O_7(s)$, $Ba_2U_3O_{11}(s)$, $Ba_{2.875}UO_{5.875}(s)$ and $Ba_3UO_6(s)$ have been computed for the first time using the data obtained in the present study and other available experimental data.

1. Introduction

During fission of uranium, a variety of fission products are formed; oxides of some of them are soluble in $UO_2(s)$ fuel, but barium oxide has a low solubility in $UO_2(s)$, because of its large ionic radius. Thus, it forms various kinds of ternary oxides [1–6]. In Ba–U–O system, several compounds have been identified in which uranium is in the six valency state. Knowledge of the thermodynamic properties of these compounds is of importance for the study of the relative stabilities of different barium uranates that may form within the $UO_2(s)$ fuel under the operating condition of the nuclear reactor. In this study low temperature heat capacity and enthalpy increments of $BaU_2O_7(s)$, $Ba_2U_3O_{11}(s)$, $Ba_{2.875}UO_{5.875}(s)$ and $Ba_3UO_6(s)$ have been measured using a Differential Scanning Calorimeter (DSC) and a Calvet calorimeter.

2. Experimental

2.1. Material preparation

Hexavalent barium uranates were prepared by the reaction of stoichiometric mixture of $BaCO_3(s)$ and $U_3O_8(s)$ in air. Barium carbonate (E. Merck, India, mass fraction purity 0.995) and U_3O_8 (nuclear grade purity supplied by nuclear Fuel Complex, Hyderabad, India) were dried by heating at 800 K in air for 5 h. Homogeneous mixtures of $BaCO_3(s)$ and $U_3O_8(s)$ in the mole ratio 3:2, 2:1, 8.625:1 and 9:1 were prepared separately for $BaU_2O_7(s)$, $Ba_2U_3O_{11}(s)$, $Ba_{2.875}UO_{5.875}(s)$ and $Ba_3UO_6(s)$, by mixing thoroughly in an agate mortar. These mixtures were separately pressed into pellets at the pressure of 100 MPa and the pellets were kept in a platinum crucible and heated at 1300 K in air for 200 h with intermediate grinding and mixing. The reaction products were analyzed by STOE, Germany, X-ray diffractometer using Cu Kα radiation. The diffraction angle 2θ (°) and the relative intensity (I/I_0) (arbitrary unit) of $BaU_2O_7(s)$, $Ba_2U_3O_{11}(s)$, $Ba_{2.876}UO_{5.875}(s)$ and $Ba_3UO_6(s)$ are separately given in Table 1 and their X-ray diffraction patterns in relation to $BaCO_3(s)$ and $U_3O_8(s)$ are given in Fig. 1. It gives evidence that the compounds used for calorimetric studies were exclusively $BaU_2O_7(s)$ [3], $Ba_2U_3O_{11}(s)$ [1], $Ba_{2.875}UO_{5.875}(s)$ [5] and $Ba_3UO_6(s)$ [6]. Pellets weighing 30–40 mg were made separately of different barium uranates and stored in the desiccator for heat capacity and enthalpy increment measurements.

2.2. Differential scanning calorimeter

Heat capacity measurements were carried out using a heat flux type DSC, DSC-131 supplied by SETARAM Instrumentation, France. The detailed experimental procedure and principle of DSC-131 have been described earlier [7]. Heat capacities of $BaU_2O_7(s)$, $Ba_2U_3O_{11}(s)$, $Ba_{2.875}UO_{5.875}(s)$ and $Ba_3UO_6(s)$ were measured in continuous mode. In this mode, temperature was increased continuously from 126–304 K. The molar heat capacities were measured with identical experimental conditions in the three runs. In the first run, two empty identical aluminium crucibles of identical masses (1.03×10^{-3} g) and volume (10^{-4} dm^3) capacity with covering lid were kept in the sample and reference cells and the heat flow versus temperature was recorded. In the second run, the heat flow versus temperature was recorded by loading NIST synthetic sapphire (SRM-720) in the powder form (200 mg) into the aluminium crucible in the sample cell keeping the crucible in the reference cell empty. In the third run, heat flow versus temperature was measured by loading the actual experimental sample (200 mg) in the powder form into the aluminium crucible in the sample side and keeping the crucible in the reference side empty. In all three sets of experiments, high purity helium as a carrier gas

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doi:10.1016/j.jnucmat.2010.06.019

Table 1
The observed 2θ (°) and relative intensities of X-ray diffraction patterns of BaU_2O_7(s), $Ba_2U_3O_{11}$(s), $Ba_{2.875}UO_{5.875}$(s) and Ba_3UO_6(s).

Compounds	2θ (°)	Relative intensity 100·(I/I_0)	Compounds	2θ (°)	Relative intensity 100·(I/I_0)
BaU_2O_7(s)	14.42	50	$Ba_{2.875}UO_{5.875}$(s)	17.34	40
	23.09	14		19.86	34
	24.81	4		25.94	21
	25.61	42		28.56	100
	28.91	100		33.77	16
	29.14	89		40.40	16
	39.75	12		41.15	42
	44.37	12		44.58	14
	46.56	17		50.19	39
	47.16	15		50.67	21
	51.24	20		59.03	12
	52.64	18		62.25	12
	54.47	8			
	60.01	19			
	61.64	8			
	66.75	7			
$Ba_2U_3O_{11}$(s)	13.29	26	Ba_3UO_6(s)	17.24	26
	14.17	10		19.89	12
	21.47	6		28.46	100
	26.94	100		33.29	14
	27.20	14		40.30	19
	28.08	81		41.14	20
	31.01	40		44.27	10
	32.08	8		50.18	43
	33.23	5		55.80	6
	34.99	5		59.03	16
	39.85	3		61.21	12
	44.37	20		62.4	12
	46.85	14		66.17	11
	48.91	23			
	53.82	5			
	54.90	15			
	55.62	8			
	57.79	8			

with the flow rate of 50 $dm^3\,min^{-1}$ and furnace heating rate of 5 K min^{-1} was maintained. At least three runs were carried out for each barium uranate.

2.3. Calvet calorimeter

The enthalpy increment measurements of BaU_2O_7(s), $Ba_2U_3O_{11}$(s), $Ba_{2.875}UO_{5.875}$(s) and Ba_3UO_6(s) were carried out using a high-temperature Calvet calorimeter model HT-1000, SETARAM, France [8]. It is a heat flow isothermal calorimeter with massive blocks of alumina to maintain constant temperature. It has two cavities surrounded by identical Pt/Pt–Rh thermopile capable of detecting heat change of 2.5 mJ. Two identical one end closed alumina tubes attached to a sample introducer were placed in these cavities. The sample was maintained at 298.15 K using water bath. Dry air atmosphere was maintained over the sample and reference chambers. The sample was held at temperature until the thermopile output signal became constant. The calorimeter was calibrated using NBS standard reference material (SRM-720), synthetic sapphire. Weighed amounts of reference material were dropped from 298.15 K into the reference side of the calorimeter kept at experimental temperature. After completion of reference run, weighed amounts of different barium uranates were dropped at same temperature into the sample side. The measurements with the sample were carried out two to three times to check the reproducibility. This procedure was repeated for BaU_2O_7(s), $Ba_2U_3O_{11}$(s), $Ba_{2.875}UO_{5.875}$(s) and Ba_3UO_6(s), separately.

3. Results

3.1. Heat capacities

The heat capacities of BaU_2O_7(s), $Ba_2U_3O_{11}$(s), $Ba_{2.875}UO_{5.875}$(s) and Ba_3UO_6(s) have been measured in the temperature range

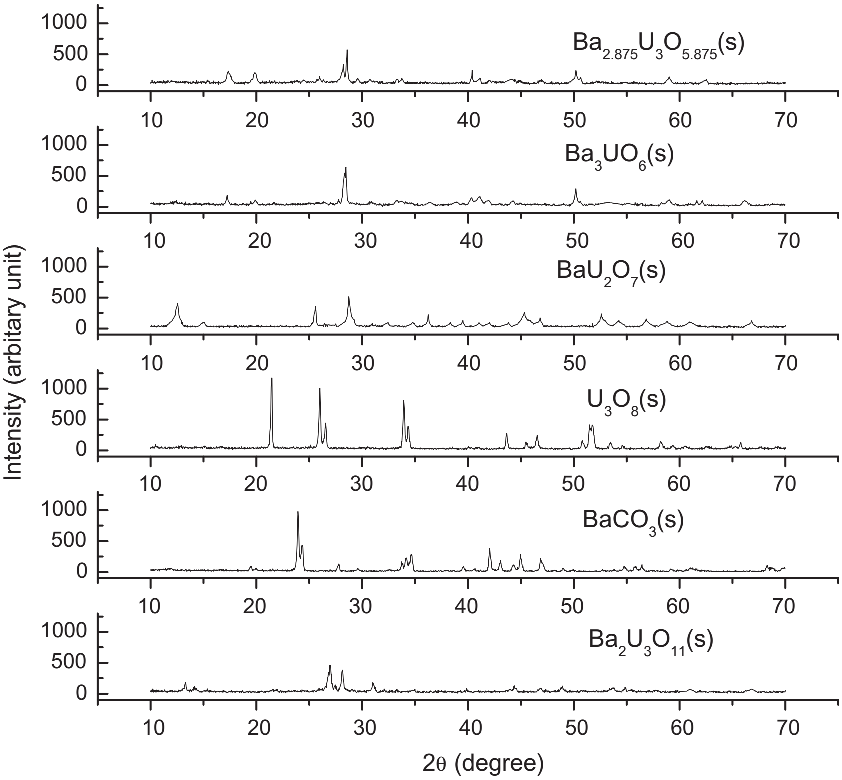

Fig. 1. X-ray diffraction pattern of $Ba_2U_3O_{11}$(s), $BaCO_3$(s), U_3O_8(s), BaU_2O_7(s), Ba_3UO_6(s) and $Ba_{2.875}UO_{5.875}$(s) are plotted with the intensity, I (arbitrary units) of peaks in y axis and the diffraction angle 2θ (°) in x axis.

126–304 K and are given in Tables 2–5. Low temperature heat capacity expressions for $BaU_2O_7(s)$, $Ba_2U_3O_{11}(s)$, $Ba_{2.875}UO_{5.875}(s)$ and $Ba_3UO_6(s)$ have been calculated by least squares analysis of the data. The uncertainties in the heat capacity measurements are within 3%. The expressions are given below where T is in K:

$BaU_2O_7(s)$

$$C^o_{p,m}(T)/\text{J K}^{-1}\cdot\text{mol}^{-1} = 308.30 - 0.89662\cdot(T/\text{K}) - 2.64\cdot 10^{-3}\cdot(T/\text{K})^2 - 2.48\cdot 10^{-6}\cdot(T/\text{K})^3 - 17.485\cdot 10^5\cdot(\text{K}/T)^2. \quad (1)$$

$Ba_2U_3O_{11}(s)$

$$C^o_{p,m}(T)/\text{J K}^{-1}\ \text{mol}^{-1} = 532.72 - 1.09638\cdot(T/\text{K}) + 1.84\cdot 10^{-3}\cdot(T/\text{K})^2 - 1.26\cdot 10^{-7}\cdot(T/\text{K})^3 - 35.757\cdot 10^5\cdot(\text{K}/T)^2. \quad (2)$$

$Ba_{2.875}UO_{5.875}(s)$

$$C^o_{p,m}(T)/\text{J K}^{-1}\ \text{mol}^{-1} = 81.50 + 1.19327\cdot(T/\text{K}) - 4.43\cdot 10^{-}3\cdot(T/\text{K})^2 + 6.66\cdot 10^{-6}\cdot(T/\text{K})^3 - 43.170\cdot 10^4\cdot(\text{K}/T)^2. \quad (3)$$

$Ba_3UO_6(s)$

$$C^o_{p,m}(T)/\text{J K}^{-1}\ \text{mol}^{-1} = 326.11 - 1.11836\cdot(T/\text{K}) + 3.00\cdot 10^{-3}\cdot(T/\text{K})^2 - 1.12\cdot 10^{-6}\cdot(T/\text{K})^3 - 11.931\cdot 10^5\cdot(\text{K}/T)^2 \quad (4)$$

3.2. Enthalpy increments

The enthalpy increment values measured at different temperatures are also given in Tables 2–5. The Shomate method [9] was used to fit these data into polynomial expressions. The constraints used were $C^o_{p,m}$ (298.15 K) = known value and $H^o_m(T) - H^o_m$ (298.15 K) = 0 at 298.15 K. The $C^o_{p,m}$(298.15 K) values measured in this study have been used for Shomate fittings. The experimental $C^o_{p,m}$(298.15 K) values for $BaU_2O_7(s)$, $Ba_2U_3O_{11}(s)$, $Ba_{2.875}UO_{5.875}(s)$ and $Ba_3UO_6(s)$ are 190.4, 325.84, 215.04 and 216.27 J K^{-1} mol^{-1}, respectively. The fit values along with the percentage difference between the experimental and calculated data for $BaU_2O_7(s)$, $Ba_2U_3O_{11}(s)$, $Ba_{2.875}UO_{5.875}(s)$ and $Ba_3UO_6(s)$ are also given in Tables 2–5.

The first differential of enthalpy increment equations with temperature for $BaU_2O_7(s)$, $Ba_2U_3O_{11}(s)$, $Ba_{2.875}UO_{5.875}(s)$ and $Ba_3UO_6(s)$ have yield heat capacity equations. Both enthalpy increments and heat capacity expressions for these barium uranates are given below.

$BaU_2O_7(s)$

$$H^o_m(T) - H^o_m(298.15\ \text{K})/\text{J mol}^{-1} = -79{,}311 + 214.51\cdot(T/\text{K}) + 30.627\cdot 10^{-3}\cdot(T/\text{K})^2 + 37.665\cdot 10^5(\text{K}/T), (299 \leqslant T/\text{K} \leqslant 1000) \quad (5)$$

$$C^o_{p,m}(T)/\text{J K}^{-1}\ \text{mol}^{-}1 = 214.51 + 61.254\cdot 10^{-3}\cdot(T/\text{K}) - 37.665\cdot 10^5\cdot(\text{K}/T), \quad (6)$$

$Ba_2U_3O_{11}(s)$

$$H^o_m(T) - H^o_m(298.15\ \text{K})/\text{J mol}^{-1} = -143{,}371 + 396.40\cdot(T/\text{K}) + 15.547\cdot 10^{-3}\cdot(T/\text{K})^2 + 70.966\cdot 10^5\cdot(\text{K}/T), \quad (324 \leqslant T/\text{K} \leqslant 1000) \quad (7)$$

$$C^o_{p,m}(T)/\text{J K}^{-1}\ \text{mol}^{-1} = 396.40 + 31.094\cdot 10^{-}3\cdot(T/\text{K}) + 4.749\cdot 10^{-}3\cdot(T/\text{K}) - 70.966\cdot 10^5\cdot(\text{K}/T)^2, \quad (8)$$

Table 2
Heat capacities and enthalpy increments of $BaU_2O_7(s)$.

Low temperature heat capacity data		T/K	$H^o(T) - H^o$(298.15 K) (J mol^{-1})			$C^o_{p,m}(T)$ (J K^{-1} mol^{-1})
T (K)	$C^o_{p,m}(T)$ (J K^{-1} mol^{-1})		Exp	Cal	% difference[a]	
126.9	123.33	298.9	143	143	0.00	190.7
134.2	132.96	300.9	525	525	0.00	191.3
141.7	139.51	313.4	2916	2942	−0.89	195.4
149.2	146.69	316.5	3508	3549	−1.17	196.3
156.7	151.65	323.7	4909	4970	−1.24	198.4
164.3	156.34	350.4	10,342	10,362	−0.19	205.3
171.8	160.24	425.9	26,975	26,447	1.96	219.8
179.4	164.23	463.5	35,473	34,819	1.84	225.4
187.1	166.97	483.1	39,949	39,262	1.72	228.0
194.8	169.89	513.9	47,085	46,342	1.58	231.7
202.5	171.9	525.1	49,692	48,945	1.50	233.0
210.2	173.73	580.6	62,861	62,044	1.30	238.9
217.9	175.5	635.1	75,978	75,207	1.01	244.1
225.7	177.4	669	84,196	83,532	0.79	247.1
233.4	178.89	685.4	88,195	87,596	0.68	248.5
241.2	181.16	760.1	106,577	106,387	0.18	254.5
248.9	182.32	800	116,454	116,605	−0.13	257.6
256.7	183.44	823.6	122,313	122,706	−0.32	259.4
264.5	184.95	865.7	132,814	133,692	−0.66	262.5
272.3	186.44	940.7	151,656	153,583	−1.27	267.9
280	187.84	973.1	160,070	162,299	−1.39	270.1
287.8	189.1	1000	166,609	169,590	−1.79	272.0
295.6	189.89					
303.4	190.9					

[a] % difference = {(Exp − Cal)/Exp}·100.

Table 3
Heat capacities and enthalpy increments of $Ba_2U_3O_{11}(s)$.

Low temperature heat capacity data		T (K)	$H^o(T) - H^o(298.15\ K)$ (J mol^{-1})			$C^o_{p,m}(T)$ (J K^{-1} mol^{-1})
T (K)	$C^o_{p,m}(T)$ (J K^{-1} mol^{-1})		Exp	Cal	% difference[a]	
126.8	200.34	323.4	8538	8530	0.09	338.6
134.1	220.83	333.9	11,959	11,974	−0.13	343.1
141.6	234.84	343.8	15,353	15,391	−0.25	347.1
149.1	248.85	373.9	25,990	25,997	−0.03	357.3
156.6	258.78	376	26,734	26,748	−0.05	357.9
164.2	268.71	423.9	44,298	44,198	0.23	370.1
171.8	277.43	473.1	62,811	62,646	0.26	379.4
179.4	283.93	523.1	82,002	81,807	0.24	386.7
187	289.13	547.8	91,559	91,398	0.18	389.8
194.8	294.97	573.6	101,618	101,492	0.12	392.7
202.4	297.94	598.4	111,350	111,262	0.08	395.2
210.2	300.82	623.9	121,418	121,370	0.04	397.6
217.9	304.34	673.1	141,048	141,034	0.01	401.7
225.6	306.66	722.3	160,855	160,886	−0.02	405.3
233.4	309.63	773.6	181,678	181,763	−0.05	408.6
241.2	311.40	824.2	202,367	202,514	−0.07	411.6
248.9	313.72	876.3	223,815	224,032	−0.10	414.4
256.7	315.48	949	254,002	254,293	−0.11	418.0
264.5	319.28	999.9	275,254	275,632	−0.14	420.4
272.3	320.12					
280.1	321.88					
287.9	323.00					
295.7	325.41					
303.5	326.54					

[a] % difference = {(Exp − Cal)/Exp}·100.

$Ba_{2.875}UO_{5.875}(s)$

$$H^o_m(T) - H_{m^o}(298.15\ \mathrm{K})/\mathrm{J\ mol^{-1}} = -108{,}672 + 287.64 \cdot (T/\mathrm{K}) + 4.749 \cdot 10^{-3} \cdot (T/\mathrm{K})^2 + 67.054 \cdot 10^5 (T/\mathrm{K}), \quad (307 \leqslant T/\mathrm{K} \leqslant 1011)$$

$$C^o_{p,m}(T)/\mathrm{J\ K^{-1}\ mol^{-1}} = 287.64 + 9.498 \cdot 10^{-3} \cdot (T/\mathrm{K}) - 67.054 \cdot 10^5 \cdot (T/\mathrm{K})^2, \qquad (10)$$

$Ba_3UO_6(s)$

$$H^o_m(T) - H^o_m(298.15\ \mathrm{K})/\mathrm{J\ mol^{-1}} = -119{,}652 + 307.12 \cdot (T/\mathrm{K}) + 37.394 \cdot 10^{-4} \cdot (T/\mathrm{K})^2 + 82.742 \cdot 10^5 \cdot (\mathrm{K}/T), \quad (302 \leqslant T/\mathrm{K} \leqslant 1012) \qquad (11)$$

$$C^o_{p,m}(T)/\mathrm{J\ K^{-1}\ mol^{-1}} = 307.12 + 7.4788 \cdot 10^{-3} \cdot (T/\mathrm{K}) - 82.742 \cdot 10^5 \cdot (\mathrm{K}/T)^2. \qquad (12)$$

Table 4
Heat capacities and enthalpy increments of $Ba_{2.875}UO_{5.875}(s)$.

Low temperature heat capacity data		T (K)	$H^o(T)$-$H^o(298.15\ K)$ (J mol^{-1})			$C^o_{p,m}(T)$ (J K^{-1} mol^{-1})
T (K)	$C^o_{p,m}(T)$ (J K^{-1} mol^{-1})		Exp	Cal	% difference[a]	
127	148.73	306.1	1704	1725	0.09	219.0
134.2	153.15	309.2	2388	2407	−0.13	220.4
141.8	159.14	318.5	4473	4476	−0.25	224.6
149.2	163.77	319.6	4725	4723	−0.03	225.0
156.8	168.31	325.8	6157	6127	−0.05	227.6
164.3	171.71	334.0	8108	8006	0.23	230.7
171.9	175.31	359.6	14,321	14,024	0.26	239.2
179.5	177.35	375.9	18,248	17,961	0.24	243.8
187.2	179.95	398.2	24,274	23,459	0.18	249.1
194.8	184.08	423.8	30,685	29,905	0.12	254.3
202.5	185.79	448.1	37,077	36,137	0.08	258.5
210.2	188.16	473.7	43,616	42,804	0.04	262.3
217.9	189.92	498.5	50,006	49,348	0.01	265.4
225.7	193.68	529.3	58,015	57,575	−0.02	268.7
233.4	196.6	573.4	69,620	69,516	−0.05	272.7
241.2	197.86	623.8	83,075	83,355	−0.07	276.3
249	200.01	673.1	96,430	97,052	−0.10	279.2
256.7	201.72	734.5	113,324	114,291	−0.11	282.2
264.5	203.46	773.4	124,175	125,299	−0.14	283.8
272.3	205.98	799.0	131,379	132,576	−0.91	284.7
280.1	208.18	848.2	145,360	146,626	−0.87	286.4
287.9	211.08	923.8	167,193	168,361	−0.70	288.6
295.7	214.65	930.1	169,632	170,179	−0.68	288.7
303.5	216.8	939.6	171,809	172,924	−0.65	289.0
		948.3	174,359	175,439	−0.62	289.2
		1006.3	191,499	192,252	−0.39	290.6
		1010.6	192,779	193,502	−0.38	290.7

[a] % difference = {(Exp − Cal)/Exp}·100.

4. Discussion

4.1. Enthalpy increment and heat capacity values

Enthalpy increment values for $BaU_2O_7(s)$, $Ba_2U_3O_{11}(s)$, $Ba_{2.875}UO_{5.875}(s)$ and $Ba_3UO_6(s)$ have not been previously reported in the literature. Enthalpy increment and heat capacity values for $BaUO_4(s)$ have been reported in the literature [10–14]. The $C^o_{p,m}(T)$ value per gram of $BaU_2O_7(s)$, $Ba_2U_3O_{11}(s)$, $Ba_{2.875}UO_{5.875}(s)$ and $Ba_3UO_6(s)$ and $BaUO_4(s)$ have been estimated from component oxides by additive oxide method using heat capacity data for $BaO(s)$ [15] and $UO_3(s)$ [15] and from experimental $H^o_m(T) - H^o_m(298.15\ K)$ values. These values are plotted against temperature in Figs. 2 and 3, respectively. It can be seen from the Fig. 2 that specific heat capacity values for $BaU_2O_7(s)$, $Ba_2U_3O_{11}(s)$, $Ba_{2.875}UO_{5.875}(s)$ and $Ba_3UO_6(s)$ calculated from additive oxide methods fall between that of $BaO(s)$ and $UO_3(s)$. The specific heat capacity of $BaO(s)$ is higher than that of $UO_3(s)$ below 600 K; thereafter the trend is reversed. Similar trends were observed for the estimated specific heat capacities of barium uranates. However, Fig. 3 shows that experimental specific heat capacity data (above 298.15 K) for all barium uranates are higher than that of $BaO(s)$ and $UO_3(s)$ and also specific heat capacities of corresponding estimated values shown in Fig. 2. Deviation of experimental specific heat capacity data of these barium uranates increases with mole fraction of $BaO(s)$ in $BaUO_4(s)$. As the mole fraction of $UO_3(s)$ in $BaUO_4(s)$ increases, the deviation of experimental specific heat capacity from component oxides becomes lower. Hence, heat capacities of $BaU_2O_7(s)$ are closer to additive oxide values than for $Ba_2U_3O_{11}(s)$. The specific heat capacity values of $Ba_3UO_6(s)$ are 11–17% higher than that calculated from the additive oxide method. Similarly, specific heat capacity for $BaU_2O_7(s)$ is about 2–3% higher than that of additive oxide method.

In order to generate thermodynamic functions for $BaU_2O_7(s)$, $Ba_2U_3O_{11}(s)$, $Ba_{2.875}UO_{5.875}(s)$ and $Ba_3UO_6(s)$ from enthalpy increment data, $\Delta_f H^o_m(298.15\ K)$ and $S^o_m(298.15\ K)$ values are required. In the Ba–U–O system, $BaUO_4(s)$, $BaU_{6.24}O_{19.7}(s)$, $BaU_2O_7(s)$, $Ba_2U_3O_{11}(s)$, $Ba_{2.875}UO_{5.875}(s)$ and $Ba_3UO_6(s)$ are stoichiometric compounds with uranium in its hexavalent state. Of these compounds, experimental $\Delta_f H^o_m(298.15\ K)$ data exist only for $BaUO_4(s)$, $BaU_2O_7(s)$ and $Ba_3UO_6(s)$. The enthalpy of formation of $BaUO_4(s)$ has been measured by O'Hare et al. [16] whereas $\Delta_f H^o_m(298.15\ K)$ of $BaU_2O_7(s)$ and $Ba_2U_2O_7(s)$ have been measured by Cordfunke and Ouwelties [17]. Experimental $\Delta_f H^o_m(298.15\ K)$ of $Ba_2U_3O_{11}(s)$ and $BaU_{6.24}O_{19.7}(s)$ have not been reported. However, present authors have calculated $\Delta_f H^o_m(Ba_2U_3O_{11},\ s,\ 298.15\ K)$ as -5237.2 kJ mol^{-1} by method suggested by Chen et al. [18] and Dash et al. [19] have estimated $\Delta_f H^o_m(298.15\ K)$ for $BaU_{6.24}O_{19.7}(s)$. Gels and Fuger [20] measured the enthalpy of formation of $Ba_3UO_6(s)$ as a part of study of the stability of hexavalent actinides in octahedral oxide co-ordination. The enthalpy of formation of $Ba_3UO_6(s)$ has been reported in Ref. [21]. Morss et al. [22] have published the enthalpy of solution of $Ba_3UO_6(s)$ in 1 M HCl. Grenthe et al. [12] have recalculated $\Delta_f H^o_m$ *(298.15 K) of $Ba_3UO_6(s)$ by taking selected auxiliary data. This value is -3210.4 ± 8 kJ mol^{-1}. The situation with respect to $S^o_m(298.15\ K)$ is poor. Experimental $S^o_m(BaUO_4,\ s,\ 298.15\ K)$ has been reported [11,12,23,24]; the other compounds in this system have to be calculated.*

4.2. Calculations of S^o_m (298.15 K) of stoichiometric oxides of barium and uranium

The entropy of a substance at any temperature can be calculated from the following relation:

$$S^o_m(298.15) = S^o_m(0) + \int_0^{298.15\ K} \{C^o_{p,m}(T)/T\} \cdot dT \tag{13}$$

Applying the third law of thermodynamics that is the entropy of any ordered crystalline substance at 0 K is zero, Eq. (13) becomes:

$$S^o_m(298.15) = \int_0^{298.15\ K} \{C^o_{p,m}(T)/T\} \cdot dT. \tag{14}$$

$C^o_{p,m}$ (T) expressions in the temperature range 0–298.15 K are required for the calculations of entropy at 298.15 K. But it is difficult to measure $C^o_{p,m}$ (T) in the neighborhoods of 0 K. Debye equation for

Table 5
Heat capacities and enthalpy increments of $Ba_3UO_6(s)$.

Low temperature heat capacity data		T (K)	$H^o(T) - H^o(298.15\ K)$ (J mol^{-1})			$C^o_{p,m}(T)$ (J K^{-1} mol^{-1})
T (K)	$C^o_{p,m}(T)$ (J K^{-1} mol^{-1})		Exp	Cal	% difference[a]	
127.1	155.74	302	837	837	0.00	218.7
134.3	161.23	306.1	1738	1739	-0.06	221.1
141.8	166.21	307.2	1980	1982	-0.10	221.7
149.3	168.87	310.3	2668	2673	-0.19	223.5
156.8	171.70	332	7691	7646	0.59	234.5
164.3	173.62	350.4	12,078	12,036	0.35	242.4
171.9	176.45	410.1	27,329	27,103	0.83	261.0
179.5	177.70	498.5	51,322	50,975	0.68	277.6
187.2	180.19	529.3	59,807	59,587	0.37	281.5
194.9	181.94	560.1	68,403	68,312	0.13	284.9
202.5	184.43	569.3	70,979	70,937	0.06	285.8
210.2	186.72	598.1	79,127	79,208	-0.10	288.5
218.0	188.48	673.1	100,823	101,057	-0.23	293.9
225.7	190.23	744.8	121,919	122,275	-0.29	297.8
233.4	192.03	754	124,632	125,016	-0.31	298.2
241.2	194.67	818.5	143,892	144,340	-0.31	300.9
249.0	197.15	828.7	148,944	147,411	1.03	301.3
256.8	200.13	848.2	152,798	153,293	-0.32	302.0
264.6	202.08	924.9	176,121	176,548	-0.24	304.4
272.2	204.75	933.3	178,678	179,106	-0.24	304.6
280.0	208.12	999.1	198,911	199,206	-0.15	306.3
287.8	210.94	1011.6	202,761	203,037	-0.14	306.6
295.6	214.99					
303.3	218.99					

[a] % difference = {(Exp − Cal)/Exp}·100.

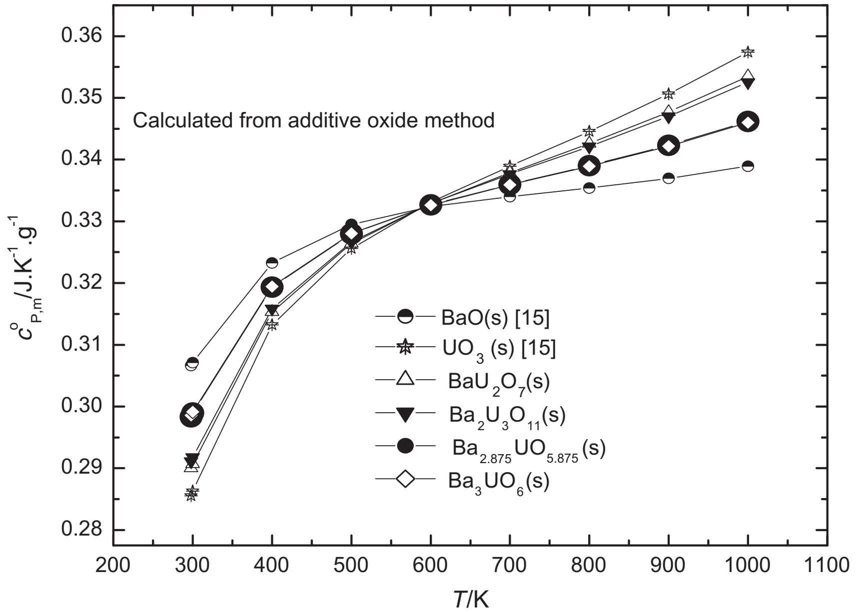

Fig. 2. A comparison of specific heat capacity data of barium uranates estimated from component oxides in this study along with that of BaO(s)[15] and UO_3(s)[15].

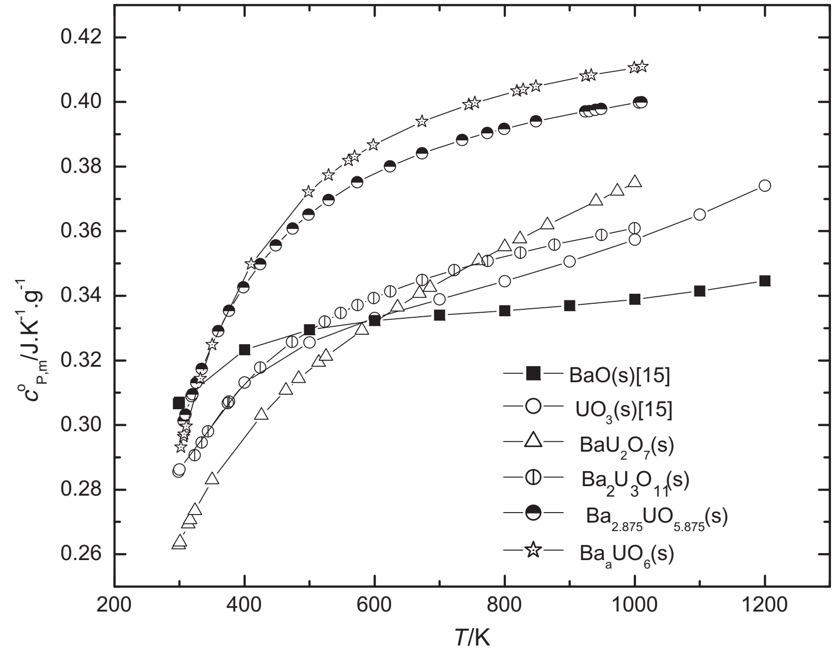

Fig. 3. A comparison of experimental specific heat capacity data of barium uranates measured in this study with that of component oxides: BaO(s) [15] and UO_3(s) [15].

the molar heat capacity of a solid at constant volume can be applied which is based upon the assumption that a crystalline solid has the properties of a perfectly elastic body and is given as:

$$C_V = \frac{9Nk_B}{x_D^3}\left(\frac{4}{15}\pi^4\right) = \frac{12}{5}Nk_B\left(\frac{T}{\theta_D}\right)^3 \quad (15)$$

where θ_D is Debye temperature, a characteristic constant for the solid can be generally derived from the slope of the experimental $C^o_{p,m}$ (T) curve above 10 K. This enables the heat capacity curve to be extrapolated to absolute zero for the relationship between heat capacity at constant volume and pressure being known. Debye's equation cannot be applied at higher temperatures. In order to use this expression experimental heat capacity around 10 K is required. However, present study measures heat capacity above 126 K. The heat capacity data on BaU_2O_7(s), $Ba_2U_3O_{11}$(s), $Ba_{2.875}UO_{5.875}$(s) and Ba_3UO_6(s) have not been reported in the literature in the temperature range 0–127 K. However, heat capacity for $BaUO_4$(s) [14] has been reported in the temperature range 0.7–292 K and that for BaO(s) [25] and UO_3(s) [26] in the temperature range 1.4–310 K and 5–350 K, respectively. The molar heat capacity of BaU_2O_7(s), $Ba_2U_3O_{11}$(s), $Ba_{2.875}UO_{5.875}$(s), Ba_3UO_6(s) and $BaUO_4$(s) calculated from the addition of the molar heat capacity of the component oxides are around 7% higher than the experimentally determined $C^o_{p,m}$ ($Ba_xU_yO_{x+3y}$, s, T) data {where (x, y) = (1, 2), (2, 3), (2.875, 1), (3, 1) or (1, 1)}. $C^o_{p,m}$(T) of BaU_2O_7(s),

$Ba_2U_3O_{11}$(s), $Ba_{2.875}UO_{5.875}$(s) and Ba_3UO_6(s) calculated from the addition of the molar heat capacity of the ternary oxide ($BaUO_4$(s)) and binary oxide (UO_3(s) or BaO(s)) are less than 5% above 127 K. Hence, it has been decided to calculate $C^o_{p,m}(Ba_xU_yO_{x+3y}, s, T)$ by addition of heat capacity of $BaUO_4$(s) and UO_3(s) or BaO(s) above 10 K. The $S^o_m(298.15)$ values for BaU_2O_7(s), $Ba_2U_3O_{11}$(s), $Ba_{2.875}UO_{5.875}$(s) and Ba_3UO_6(s) can now be computed by evaluating integrals of Eq. (16):

$$S^o_m(298.15) = \int_0^{T1} \{C^o_{p,m}(T)/T\} \cdot dT + \int_{T1}^{T2} \{C^o_{p,m}(T)/T\} \cdot dT + \int_{T2}^{298.15\text{ K}} \{C^o_{p,m}(T)/T\} \cdot dT \qquad (16)$$

To derive the standard entropy at $T = 298.15$ K, heat capacity expressions in various temperature ranges ($0–T_1$, $T_1–T_2$ and T_2–298.15 K, where $T_1 = 10$ K and $T_2 = 127$ K) for BaU_2O_7(s), $Ba_2U_3O_{11}$(s), $Ba_{2.875}UO_{5.875}$(s) and Ba_3UO_6(s) were needed which were calculated from the overlapping polynomial curves fitting methods.

4.3. Fitting of heat capacity data

The molar heat capacity data in the temperature range 0–298.15 K have been fitted into four different polynomials. $C^o_{p,m}(T)$ data in the temperature range 127–298.15 K were taken from experimentally measured data (126–304 K) fitted into expression:

$$C^o_{p,m}(T) = a + bT + cT^2 + dT^3 + e/T^2 \qquad (17)$$

Heat capacity above 10 K was calculated from experimental heat capacity data of $BaUO_4$(s) and BaO(s) or UO_3(s) and these data along with experimental heat capacity data (127–134 K) of the present study were fitted into expression:

$$C^o_{p,m}(T) = a1 + b1T + c1T^2 + d1T^3 \qquad (18)$$

The straight line portion of heat capacities (10–25 K) of Eq. (18) were fitted into expression:

$$C^o_{p,m}(T) = b_2T + d_2T^3 \qquad (19)$$

where the second term gives limiting ($T = 0$ K) lattice heat capacity and the first term is ground state electronic contribution which does not vary much within an energy interval $\pm 3k_BT$ around the Fermi level. Below 10 K heat capacity was calculated as:

$$C^o_{p,m}(T) = d_2 \cdot T^3 \qquad (20)$$

The coefficient d_2 was correlated to θ_D at 0 K using Eq. (21):

$$\theta_D = [12 \cdot R \cdot \pi^4 \cdot n/5 \cdot d_2]^{1/3} = [1943.7 \cdot n/d_2]^{1/3} \qquad (21)$$

where n is number of atoms in BaU_2O_7(s), $Ba_2U_3O_{11}$(s), $Ba_{2.875}UO_{5.875}$(s) and Ba_3UO_6(s) and calculated θ_D values for these compounds are given in Table 6. The heat capacities of $Ba_xU_yO_{x+3y}$(s) were fitted in the temperature ranges 127–298.15 K, 10–127 K and 0–10 K, respectively, using Eq. (17), Eqs. (18) and (20) for the calculations of S^o_m ($Ba_xU_yO_{x+3y}$, s, 298.15 K). These values are given in Table 6 along with $C^o_{p,m}(Ba_xU_yO_{x+3y}, s, T)$ values. The $C^o_{p,m}(T)/T$ values of $Ba_xU_yO_{x+3y}$(s) were plotted as a function of temperature in Fig. 4. The area under the curve in the temperature range 0–298.15 K of each $Ba_xU_yO_{x+3y}$(s) gives the entropy value at 298.15 K. S^o_m(298.15 K) values for BaU_2O_7(s), $Ba_2U_3O_{11}$(s), $Ba_{2.875}UO_{5.875}$(s) and Ba_3UO_6(s) were also estimated by Cordfunke and Ijdo [27] by additive oxide method taking $\Delta_{ox}\ S^o_m = 0$ at 298.15 K. These estimated values are also given in the Table 6 which shows close agreement between calculated and estimated S^o_m ($Ba_xU_yO_{x+3y}$, s, 298.15 K) values.

4.4. Thermodynamic functions

The self consistent thermodynamic functions like $S^o_m(T)$, $C^o_{p,m}(T)$, $H^o_m(T)$, $\{H^o_m(T) - H^o_m(298.15\text{ K})\}$, $G^o_m(T)$, $\phi^o_m(T)$ $\{-(G^o_m(T) - H^o_m(298.15))/T\}$, $\Delta_f\ H^o_m(T)$ and $\Delta_f\ G^o_m(T)$ have been calculated in the temperature range 298.15–1200 K using selected $\Delta_f\ H^o_m$(298.15 K), S^o_m(298.15 K) and heat capacity data.

These functions for BaU_2O_7(s), $Ba_2U_3O_{11}$(s), $Ba_{2.875}UO_{5.875}$(s) and Ba_3UO_6(s) in the temperature range 298.15–1200 K are given respectively, in Tables 7–10. $\Delta_f\,G^o_m$(298.15 K) of BaU_2O_7(s) reported (−3052.1 ± 6.7 kJ mol^{-1}) in the literature [12] is matching with that (−3052.4 kJ mol^{-1}) calculated in this study. Similarly, $\Delta_f\ G^o_m(Ba_3UO_6$, s, 298.15 K) reported (−3045.0 ± 9.2 kJ mol^{-1}) in the literature [12] is also matching well with that (−3044.5 kJ mol^{-1}) given in Table 10.

Table 6

The coefficients of heat capacity expression, entropy and Debye temperature values for BaU_2O_7(s), $Ba_2U_3O_{11}$(s), $Ba_{2.875}UO_{5.875}$(s) and Ba_3UO_6(s).

Compounds	Temperature range (K)	$C^o_{p,m}(T)$ (J K^{-1} mol^{-1})					$\int C^o_{p,m}(T)/T.dT$ (J K^{-1} mol^{-1})	S^o_m(298.15) (J K^{-1} mol^{-1})	θ_D (K)	θ_D (effective) (K)
		a	$b.T$	$c.T^2 \cdot 10^3$	$d.T^3 \cdot 10^5$	$eT^2 \cdot 10^{-5}$				
BaU_2O_7(s)	0–10				35.0		0.02	260.7		
	10–126.9	− 8.983	0.80518	7.44	−4.24		104.57			
										721
	126.9–303.4	308.30	−0.89662	2.64	−0. 248	−17.485		260 ± 5[a]	380	
	126.9–298.15	308.30	−0.89662	2.64	−0. 248	−17.485	156.07			
$Ba_2U_3O_{11}$(s)	0–10				73.0		0.03	411.2	350	621
	10–126.8	−2.446	−0.16714	33.68	−15.5		138.35			
	126.8–303.5	532.72	−1.09638	1.84	−0.0126	−35.757		405 ± 5[a]		
	126.8–298.15	532.72	−1.09638	1.84	−0.0126	−35.757	272.84			
$Ba_{2.875}UO_{5.875}$(s)	0–10				74.0		0.03	281.7	294.8	578
	10–127	−9.480	0.81641	12.2	−6.88		121.87			
	127–303.5	81.497	1.19327	−4.43	0.666	−4.317				
	127–298.15	81.497	1.19327	−4.43	0.666	−4.317	159.81			
Ba_3UO_6(s)	0–10				75.0		0.03	296.5	296	619
	10–127.1	−10.1	0.88097	11.4	−6.35		129.41			
	127.1–303.3	326.11	−1.11836	3.00	−0.112	−11.931				
	127.1–298.15	326.11	−1.11836	3.00	−0.112	−11.931	167.02	298 ± 5[a]		

[a] Estimated by Cordfunke and Ijdo [27].

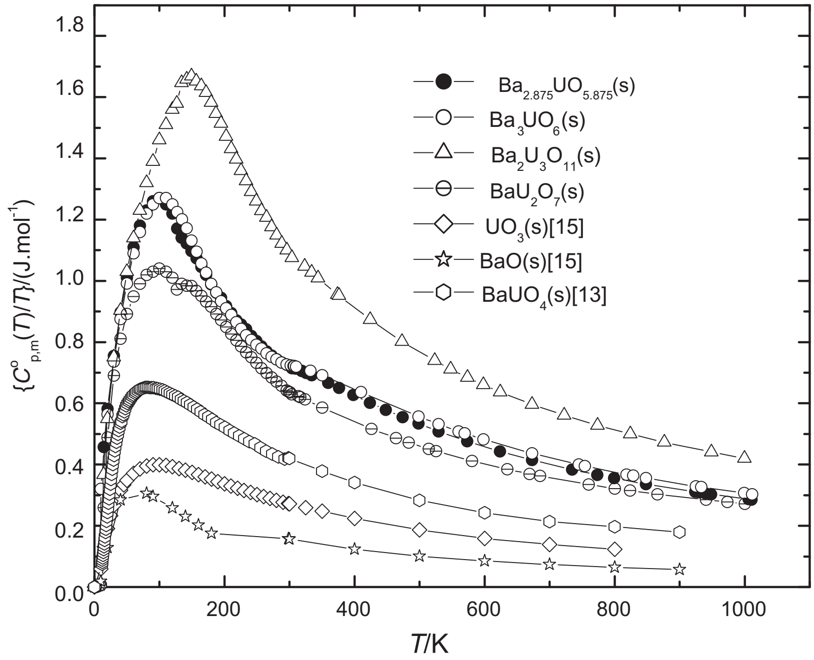

Fig. 4. A plot of $C^{o}_{p,m}(T)/T$ versus temperature of $BaU_2O_7(s)$, $Ba_2U_3O_{11}(s)$, $Ba_{2.875}UO_{5.875}(s)$ and $Ba_3UO_6(s)$ for the calculations of entropy at any particular temperature. Similar plots for $BaUO_4(s)$, BaO(s) and $UO_3(s)$ are included for comparisons.

4.5. Calculation of Debye temperature as a function of temperature

This can be calculated from heat capacity data at constant volume (C^{o}_{v}). The relationship between C^{o}_{p} and C^{o}_{v} for the solid is more complicated than for the gaseous state and is given by a formula which includes the compressibility of the solid and its thermal expansion. These quantities are not known exactly, however the difference between these two heat capacities amount only 0.8–2 J K^{-1} atom^{-1}. For barium uranates it has been assumed to be 1 J K^{-1} atom^{-1} above 25 K and C^{o}_{v} is equal to C^{o}_{p} below 25 K. The constant volume heat capacity per atom is obtained by differentiating the internal energy with respect to temperature and is given by:

Table 7
Thermodynamic functions for $BaU_2O_7(s)$.

T (K)	$C^{o}_{p,m}(T)$ (J K^{-1} mol$^{-1)}$	$S^{o}_{m}(T)$ (J K^{-1} mol^{-1})	$H^{o}_{m}(T) - H^{o}_{m}(298.15)$ (kJ mol$^{-1)}$	$\phi^{o}_{m}(T)$ (J K^{-1} mol^{-1})	$H^{o}_{m}(T)$ (kJ mol$^{-1)}$	$G^{o}_{m}(T)$ (kJ mol^{-1})	$\Delta_f H^{o}_{m}(T)$ (kJ mol^{-1})	$\Delta_f G^{o}_{m}(T)$ (kJ mol^{-1})
298.15	190.4	260.7	0.0	260.7	−3237.2	−3314.9	−3237.2	−3052.4
300	191.0	261.9	0.4	260.6	−3236.8	−3315.4	−3237.1	−3051.2
400	215.5	320.6	20.8	268.6	−3216.4	−3344.6	−3236.1	−2989.4
500	230.1	370.3	43.1	284.1	−3194.1	−3379.3	−3234.5	−2927.9
600	240.8	413.2	66.7	302.0	−3170.5	−3418.4	−3232.6	−2866.7
700	249.7	451.1	91.2	320.8	−3146	−3461.8	−3230.9	−2806.0
800	257.6	484.9	116.6	339.2	−3120.6	−3508.5	−3229.4	−2745.3
900	265.0	515.7	142.7	357.1	−3094.5	−3558.6	−3228.4	−2685.0
1000	272.0	544.0	169.6	374.4	−3067.6	−3611.6	−3232.5	−2624.3
1100	278.8	570.2	197.1	391.0	−3040.1	−3667.3	−3246.0	−2562.4
1200	285.4	594.8	225.3	407.1	−3011.9	−3725.7	−3241.9	−2500.5

Table 8
Thermodynamic functions for $Ba_2U_3O_{11}(s)$.

T (K)	$C^{o}_{p,m}(T)$ (J K^{-1}mol^{-1})	$S^{o}_{m}(T)$ (J K^{-1}mol^{-1})	$H^{0}_{m}(T) - H^{o}_{m}(298.15)$ (kJ mol^{-1})	$\phi^{o}_{m}(T)$ (J K^{-1} mol^{-1})	$H^{o}_{m}(T)$ (kJ mol^{-1})	$G^{o}_{m}(T)$ (kJ mol^{-1})	$\Delta_f H^{o}_{m}(T)$ (kJ mol^{-1})	$\Delta_f G^{o}_{m}(T)$ (kJ mol^{-1})
298.15	325.8	411.2	0.0	411.2	−5237.2	−5359.8	−5237.2	−4941.4
300	326.9	413.2	0.6	411.2	−5236.6	−5360.6	−5237.2	−4939.6
400	364.5	513.1	35.4	424.6	−5201.8	−5407.0	−5233.8	−4840.9
500	383.6	596.7	72.9	450.9	−5164.3	−5462.6	−5229.9	−4743.1
600	395.4	667.7	111.9	481.2	−5125.3	−5525.9	−5226.3	−4646.0
700	403.7	729.3	151.9	512.3	−5085.3	−5595.8	−5223.4	−4549.5
800	410.2	783.7	192.6	543.0	−5044.6	−5671.6	−5221.6	−4453.4
900	415.6	832.3	233.9	572.4	−5003.3	−5752.4	−5220.9	−4357.4
1000	420.4	876.4	275.7	600.7	−4961.5	−5837.9	−5228.8	−4261.1
1100	424.7	916.6	317.9	627.6	−4919.3	−5927.6	−5254.5	−4162.3
1200	428.8	953.8	360.6	653.3	−4876.6	−6021.2	−5250.9	−4063.2

Table 9
Thermodynamic functions for $Ba_{2.875}UO_{5.875}$(s).

T (K)	$C^o_{p,m}(T)$ (J K^{-1} mol^{-1})	$S^o_m(T)$ (J K^{-1} mol^{-1})	$H^0_m(T) - H^o_m(298.15)$ (kJ mol^{-1})	$\phi^o_m(T)$ (J K^{-1} mol^{-1})	$H^o_m(T)$ (kJ mol^{-1})	$G^o_m(T)$ (kJ mol^{-1})	$\Delta_f H^o_m(T)$ (kJ mol^{-1})	$\Delta_f G^o_m(T)$ (kJ mol^{-1})
298.15	215.04	281.7	0.0	281.7	−3137.3	−3221.3	−3137.3	−2973.2
300	215.98	283.0	0.4	281.7	−3136.9	−3221.8	−3136.9	−2972.1
400	249.53	350.4	23.9	290.7	−3113.4	−3253.6	−3113.8	−2917.5
500	265.57	408.0	49.7	308.6	−3087.6	−3291.6	−3108.9	−2863.6
600	274.71	457.3	76.8	329.3	−3060.5	−3334.9	−3128.8	−2810.2
700	280.60	500.1	104.6	350.7	−3032.7	−3382.8	−3126.2	−2757.3
800	284.76	537.9	132.9	371.8	−3004.4	−3434.7	−3124.1	−2704.7
900	287.91	571.6	161.5	392.2	−2975.8	−3490.2	−3122.5	−2652.3
1000	290.43	602.1	190.4	411.7	−2946.9	−3549.0	−3123.9	−2600.1
1100	292.55	629.9	219.6	430.3	−2917.7	−3610.6	−3145.9	−2545.6
1200	294.38	655.4	248.9	448.0	−2888.4	−3674.9	−3142.4	−2491.2

Table 10
Thermodynamic functions for Ba_3UO_6(s).

T (K)	$C^o_{p,m}(T)$ (J K^{-1} mol^{-1})	$S^o_m(T)$ (J K^{-1} mol^{-1})	$H^o_m(T) - H^o_m(298.15)$ (kJ mol^{-1})	$\phi^o_m(T)$ (J K^{-1} mol^{-1})	$H^o_m(T)$ (kJ mol^{-1})	$G^o_m(T)$ (kJ mol^{-1})	$\Delta_f H^o_m(T)$ (kJ mol^{-1})	$\Delta_f G^o_m(T)$ (kJ mol^{-1})
298.15	216.27	296.5	0.0	296.5	−3210.4	−3298.8	−3210.4	−3044.5
300	217.43	297.8	0.4	296.5	−3210.0	−3299.3	−3210.4	−3043.5
400	258.40	366.8	24.5	305.6	−3185.9	−3332.6	−3207.8	−2988.2
500	277.76	426.8	51.4	324.0	−3159.0	−3372.4	−3204.4	−2933.7
600	288.62	478.5	79.8	345.5	−3130.6	−3417.7	−3200.9	−2879.9
700	295.47	523.5	109.0	367.8	−3101.4	−3467.9	−3197.6	−2826.6
800	300.17	563.3	138.8	389.8	−3071.6	−3522.2	−3194.7	−2773.9
900	301.17	588.9	164.5	406.1	−3045.9	−3575.9	−3196.8	−2716.9
1000	303.32	615.6	192.4	423.2	−3018.0	−3633.6	−3199.9	−2660.7
1100	305.20	639.5	220.4	439.1	−2990.0	−3693.5	−3224.8	−2601.4
1200	307.57	666.1	251.1	456.9	−2959.3	−3758.6	−3220.6	−2544.8

$$C_V = \left[\frac{\partial \bar{E}}{\partial T}\right]_V = \frac{9Nk_B}{x_D^3}\int_0^{x_D}\frac{x^4e^x}{(e^x-1)^2}dx$$

$$= 9Nk_B\left(\frac{T}{\theta_D}\right)^3\int_0^{x_D}\frac{x^4e^x}{(e^x-1)^2}dx \qquad (22)$$

where $x_D = \frac{h\upsilon_D}{k_BT} = \frac{\theta_D}{T}$ (υ_D is Debye frequency and θ_D is Debye temperature) (23)

or

$$\frac{C_p-1}{3R} = \frac{3}{x^3}\int_0^{x}\frac{x^4e^x}{(e^x-1)^2}dx = f(\text{Debye}) \qquad (24)$$

where C_p is equal to $C^o_{p,m}$ $(T)/n$. From the left hand side value of Eq. (24), at any temperature, θ_D/T has been calculated from the tabulated universal Debye function. The θ_D at any temperature was calculated as the product of that temperature and x (tabulated Debye function). The θ_D for $BaUO_4$(s), UO_3(s) and BaO(s) have been

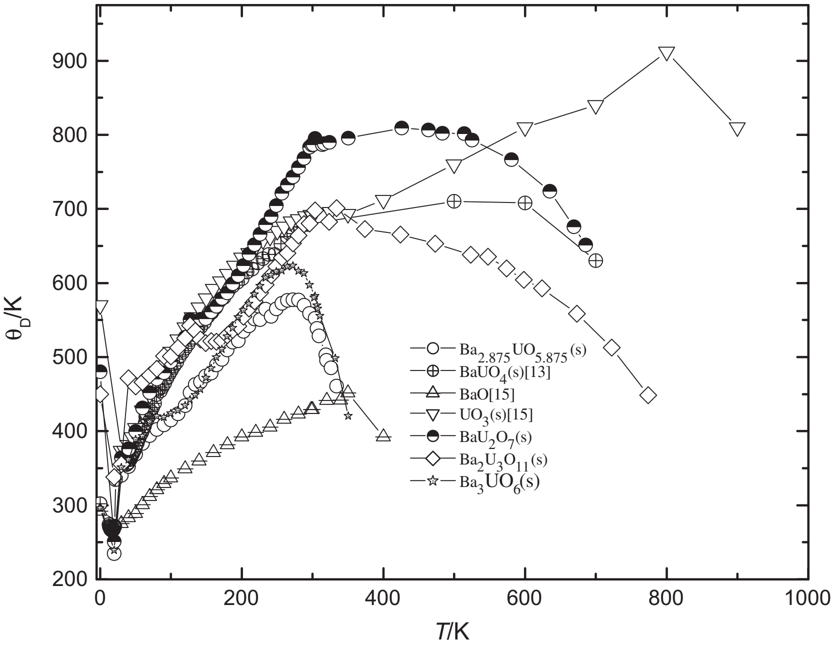

Fig. 5. A plot of Debye temperature (θ_D) against temperature for BaU_2O_7(s), $Ba_2U_3O_{11}$(s), $Ba_{2.875}UO_{5.875}$(s), Ba_3UO_6(s), $BaUO_4$(s), BaO(s) and UO_3(s).

calculated from the heat capacity data reported in the literature [13,15] and that for BaU_2O_7(s), $Ba_2U_3O_{11}$(s), $Ba_{2.875}UO_{5.875}$(s) and Ba_3UO_6(s) have been calculated from the heat capacity data of the present study.

The variation of θ_D with temperature for BaU_2O_7(s), $Ba_2U_3O_{11}$(s), $Ba_{2.875}UO_{5.875}$(s) and Ba_3UO_6(s), $BaUO_4$(s), UO_3(s) and BaO(s) have been shown in Fig. 5. This figure shows that θ_D increases with temperature till a plateau (effective Debye temperature) reaches then decreases. These temperatures of BaU_2O_7(s), $Ba_2U_3O_{11}$(s), $Ba_{2.875}UO_{5.875}$(s) and Ba_3UO_6(s) have been included in Table 6. Fig 5 shows that θ_D of BaU_2O_7(s), $Ba_2U_3O_{11}$(s) and $BaUO_4$(s) follows same trend as UO_3(s). Similarly θ_D for $Ba_{2.875}UO_{5.875}$(s) and Ba_3UO_6(s) follows that of BaO(s). The former group shows more flat variation of θ_D than the latter group. Hence anharmonicity is more prominent in $Ba_{2.875}UO_{5.875}$(s) and Ba_3UO_6(s) and heat capacity values of these barium uranates deviate from that calculated from the Newman's Kopp's rule.

5. Conclusion

Enthalpy increment values for BaU_2O_7(s), $Ba_2U_3O_{11}$(s), $Ba_{2.875}UO_{5.875}$(s) and Ba_3UO_6(s) have been measured using Calvet calorimeter. The specific heat capacity values of these compounds are higher than component oxides. The deviation between the experimental and those calculated from component oxides increases with Ba/U ratio. Thermodynamic functions and Debye temperature are generated for the first time for BaU_2O_7(s), $Ba_2U_3O_{11}$(s), $Ba_{2.875}UO_{5.875}$(s) and Ba_3UO_6(s) using required data from the literature.

Acknowledgements

The authors are thankful to Dr. V. Venugopal, Director Radiochemistry and Isotope Group for his constant encouragement during the progress of this work. Authors are also thankful to Dr. N.D. Dahale and K. Krishanan for XRD analysis.

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