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Journal of Nuclear Materials 279 (2000) 84–90

journal of nuclear materials

www.elsevier.nl/locate/jnucmat

Calorimetric studies on the strontium–uranium–oxygen system

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Received 16 March 1999; accepted 4 November 1999

Abstract

Enthalpy increment measurements on $Sr_3U_{11}O_{36}$(s) and $Sr_3U_2O_9$(s) were carried out using a Calvet micro-calorimeter. The enthalpy increment values were least squares analyzed with the constraints that $H^0(T) - H^0(298.15\ \mathrm{K})$ at 298.15 K equals zero and $C^0_{\mathrm{p,m}}(298.15\ \mathrm{K})$ equals 1064.2 and 301.8 J $\mathrm{K^{-1}mol^{-1}}$ for $Sr_3U_{11}O_{36}$(s) and $Sr_3U_2O_9$(s), respectively. The dependence of enthalpy increments with temperature can be given as

$$H^0(T) - H^0(298.15\ \mathrm{K})\ (\mathrm{J\ mol^{-1}}) = -304152 + 962.72T\ (\mathrm{K}) + 177.63 \times 10^{-3}T^2\ (\mathrm{K}) + 3.954 \times 10^5/T\ (\mathrm{K}),$$

$$(\mathrm{Sr_3U_{11}O_{36}(s)}, 299.0 \leqslant T\ (\mathrm{K}) \leqslant 1000),$$

$$H^0(T) - H^0(298.15\ \mathrm{K})\ (\mathrm{J\ mol^{-1}}) = -1\ 15\ 817 + 319.18T\ (\mathrm{K}) + 58.01 \times 10^{-3}T^2\ (\mathrm{K}) + 46.201 \times 10^5/T\ (\mathrm{K}),$$

$$(\mathrm{Sr_3U_2O_9(s)}, 299.0 \leqslant T\ (\mathrm{K}) \leqslant 1000).$$

Thermodynamic functions for $Sr_3U_{11}O_{36}$(s) and $Sr_3U_2O_9$(s), have been generated using the $\Delta_f H^0_m(298.15\ \mathrm{K})$, $\Delta_f G^0_m(T)$ and $S^0_m(298.15\ \mathrm{K})$ values, either calculated in this study or from the literature. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

Fission product strontium is formed in relatively large amounts in irradiated nuclear fuel, and it is therefore of interest to know the thermochemical stability of strontium compounds in the Sr–U–O system. In this system a number of compounds have been found [1–6]: $SrUO_3$, β-$SrUO_4$, Sr_2UO_5, Sr_3UO_6, $SrUO_{3+x}$, $Sr_2U_3O_{11}$, SrU_4O_{13}, $Sr_3U_2O_9$ and $Sr_3U_{11}O_{36}$. α-$SrUO_4$ has always been obtained at low oxygen potential having the composition $SrUO_{4-x}$ [5]. Hoekstra and Katz [7] have described a phase $SrUO_{3+x}$. Cordfunke and Loopstra [1] have found that these two phases, each being rhombohedral, co-exist between the compositions $SrUO_{3.3}$ and $SrUO_{3.75}$. Cordfunke and Loopstra [1] have mentioned that physicochemical properties of SrU_4O_{13} are closely related to that of U_3O_8. Recently Cordfunke et al. [8] have showed its composition to be slightly different, corresponding with the formula $Sr_3U_{11}O_{36}$(s). Authors [8] have also determined the crystal structure of $Sr_3U_{11}O_{36}$ by X-ray, electron and neutron diffraction techniques. In the SrO–UO_3 system, six uranates with uranium in the hexa valent state are present. Of these, the structures of $Sr_2U_3O_{11}$ and $Sr_3U_{11}O_{36}$ are closely related to α-$SrUO_4$ (rhombohedral), whereas the structures of β-$SrUO_4$, Sr_2UO_5 and Sr_3UO_6, are monoclinic. The structure of $Sr_3U_2O_9$ is not reported. Cordfunke and Loopstra [1] have measured enthalpy of solution for β-$SrUO_4$, Sr_2UO_5, Sr_3UO_6 and $Sr_2U_3O_{11}$ in nitric acid. Cordfunke and O'Hare [9] have recalculated the enthalpy of formation data of Cordfunke and Loopstra [1]. Except for β-$SrUO_4$ [10,11], low temperature heat capacity and high temperature enthalpy increment data for other ternary compounds in the Sr–U–O system are not reported. Huang et al. [12] have studied the vapourization properties of $SrUO_3$(s) using Knudsen effusion mass spectrometry in the temperature range 1534–1917 K. Cordfunke et al. [8] have determined enthalpy of formation of $Sr_3U_{11}O_{36}$(s) using solution calorimetry. Other thermodynamic details are not reported for these uranates. In the present study, the enthalpy increments for $Sr_3U_{11}O_{36}$(s) and $Sr_3U_2O_9$(s) have been determined using a high temperature Calvet calorimeter in the temperature ranges 299–1000 K.

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PII: S0022-3115(99)00271-8

2. Experimental

$Sr_3U_{11}O_{36}$(s) and $Sr_3U_2O_9$(s) were synthesized by reacting stoichiometric ratios of $SrCO_3$(s) and U_3O_8(s) at 1100 K in an alumina boat in air for about 200 h. The colour of the reaction products was reddish brown and yellowish orange for $Sr_3U_{11}O_{36}$(s) and $Sr_3U_2O_9$, respectively. The compounds obtained in the above experiments were identified exclusively as $Sr_3U_{11}O_{36}$(s) and $Sr_3U_2O_9$(s) by X-ray diffraction (XRD) analysis. The X-ray pattern was taken on a Diano X-ray diffractometer using Cu K_α radiations. The XRD patterns for $Sr_3U_{11}O_{36}$(s) and $Sr_3U_2O_9$(s) are given in Figs. 1 and 2, respectively. The observed and reported *d*-values of the major lines of X-ray patterns for $Sr_3U_{11}O_{36}$(s) and $Sr_3U_2O_9$(s) are compared with the literature in Table 1. Impurities analysis of $Sr_3U_{11}O_{36}$(s) and $Sr_3U_2O_9$(s) are given in Table 2. The major components: Sr:U ratios for $Sr_3U_{11}O_{36}$(s) and $Sr_3U_2O_9$(s) have been determined using couple plasma and X-ray fluorescnce (XRF) method. Six synthetic mixtures giving Sr/U atomic ratio: 3 to 0.2 were prepared by mixing equilibrated $UO_{2.00}$(s) and dried $SrCO_3$(s). The samples for XRF method, were prepared in the form of thin films in 10% solution of collodion in amyl acetate dispersed on 30 mm diameter filter paper. Intensities ratio: I_{Sr}/I_U were measured for each synthetic standard and plotted against the atomic ratio of Sr/U and an equation relating these two values was found by the method of least squares. On the basis of the least square equation Sr/U ratio for $Sr_3U_{11}O_{36}$(s) and $Sr_3U_2O_9$(s) were determined and values are summarized in Table 3. Tables 1–3 provided evidence that solids: $Sr_3U_{11}O_{36}$(s) and $Sr_3U_2O_9$(s) are single phase. This suggests that oxidation of U(VI), was completed. Dried samples of $Sr_3U_{11}O_{36}$(s) and $Sr_3U_2O_9$(s) were made into pellets of 4 mm diameter and 1 mm thickness under a pressure of 100 MPa. These pellets were annealed in air at 800 K for 50 h and stored in a desiccator for $H^0(T) - H^0(298.15\ K)$ measurements.

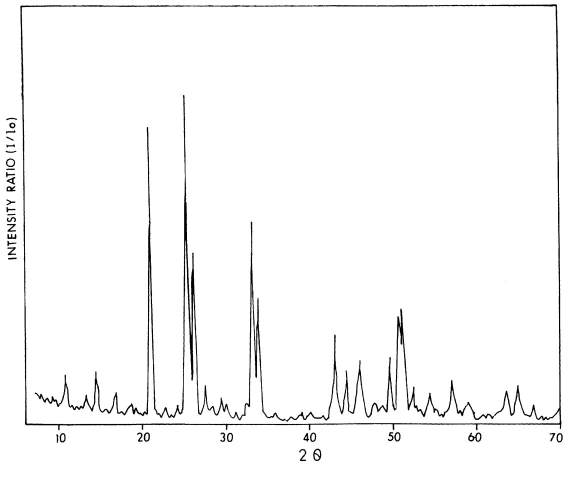

Fig. 1. XRD pattern for $Sr_3U_{11}O_{36}$(s). The intensity ratio I/I_0 as a function of 2θ, where θ is the angle between the incident X-ray beam and crystal.

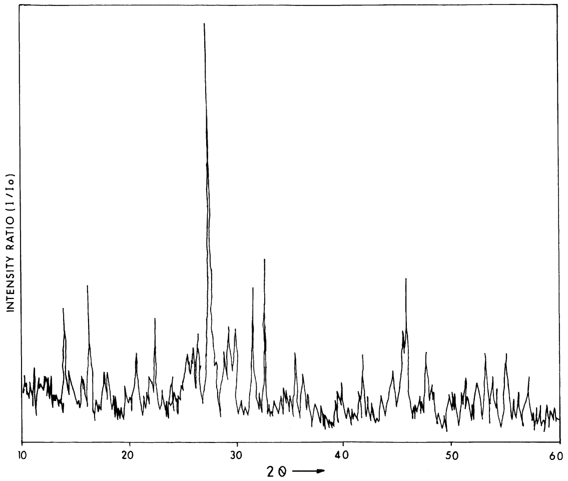

Fig. 2. XRD pattern for $Sr_3U_2O_9$(s). The intensity ratio I/I_0 as a function of 2θ, where θ is the angle between the incident X-ray beam and crystal.

The Calvet micro-calorimeter model HT-1000, supplied by SETARAM, France, has been used for enthalpy increment measurements of $Sr_3U_{11}O_{36}$(s) and $Sr_3U_2O_9$(s) using drop calorimetry. The calorimeter has an isothermal alumina block which contains two identical one end closed alumina cells surrounded by a series of thermopiles connect in opposition to detect small perturbation. The sample, in the form of a pellet, maintained at 298.15 K in the sample holder, was dropped into the sample cell maintained at the experimental temperature. The temperature of the isothermal block was measured using a platinum to (platinum + 10 mass% rhodium) thermocouple (±0.1 K). The heat flow between the isothermal block and either of the cells was recorded in the form of milli-volt signal. The details of the experimental measurements have been described elsewhere [13]. The heat calibration was carried out using synthetic sapphire [NIST SRM-720].

3. Results

The $H^0(T) - H^0(298.15\ K)$ values for $Sr_3U_{11}O_{36}$(s) and $Sr_3U_2O_9$(s) obtained at different temperatures are given in Tables 4 and 5, respectively.

The main objective of the enthalpy increment data is to derive heat capacity, an import thermodynamic function. In fitting the $H^0(T) - H^0(298.15\ K)$ values to different algebraic equations, for the same compound will result numerous value of $C_p^0(298.15\ K)$. The usual

Table 1
Comparison of observed and reported XRD patterns for $\mathrm{Sr_3U_{11}O_{36}}$(s) and $\mathrm{Sr_3U_2O_9}$(s)

Compound	Observed d value	Relative intensity	Reported [8] d-values	Relative intensity
$\mathrm{Sr_3U_{11}O_{36}}$(s)	8.12	26	9.058	25
	6.08	16	6.095	5
	4.20	91	5.264	20
	3.49	100	4.199	90
	3.37	52	3.489	100
	2.68	61	3.371	60
	2.62	38	2.682	80
	2.09	27	2.627	50
	2.03	16	2.096	40
	1.96	19	2.037	30
	1.83	20	1.965	30
	1.79	32	1.831	30
	1.78	35	1.796	50
	1.74	11	1.779	50
	1.68	10	1.743	25
	1.61	13	1.683	20
	1.56	10	1.609	25
	1.43	11	1.561	20
			1.433	30
			1.396	20

Compound	Observed d value	Relative intensity	Reported [6] d-values	Relative intensity
$\mathrm{Sr_3U_2O_9}$(s)	6.43	31	6.43	20
	5.52	35	5.52	30
	3.97	27	3.96	25
	3.38	24	3.37	10
	3.22	100	3.22	100
	2.84	34	2.80	25
	2.75	40	2.76	15
	2.51	19	2.50	10
	2.26	13	2.27	10
	2.03	15	2.07	25
	1.97	36	1.97	40
	1.87	9	1.87	10
	1.70	13	1.69	35
	1.67	19	1.67	20
	1.61	14	1.61	15

plot of experimental $H^0(T) - H^0(298.15\ \mathrm{K})$ data vs T with constraint $H^0(T) - H^0(298.15\ \mathrm{K})$ at $T = 298.15$ K is also not satisfactory for obtaining low temperature experimental $C_\mathrm{p}^0(T)$ values. To correlate smoothly $H(T) - H(298.15\ \mathrm{K})$ data with low-temperature heat capacities in neighborhood of room temperature, Shomate's method has been used. In this method, boundary conditions used are: (i) $H^0(T) - H^0(298.15\ \mathrm{K}) = 0$ at 298.15 K and (ii) $C_\mathrm{p}^0(298.15\ \mathrm{K}) =$ known value. Thus, prior knowledge of $C_\mathrm{p}^0(298.15\ \mathrm{K})$ is required for fitting $H^0(T) - H^0(298.15\ \mathrm{K})$ data by Shomate's method [14]. $C_\mathrm{p}^0(298.15\ \mathrm{K})$ value can either be estimated or determined experimentally. In absence of any experimental $C_\mathrm{p}^0(298.15\ \mathrm{K})$ data, this has been derived from our low temperature $(299 \leqslant T\ (\mathrm{K}) \leqslant 339\ \mathrm{K})$ data. The method of calculation has been described elsewhere [15]. In the mentioned temperature range $C_\mathrm{p}^0(T)$ vs T plot was a straight line. The corresponding $C_\mathrm{p,m}^0(298.15\ \mathrm{K})$ values is 1064.2 and 301.8 J $\mathrm{K^{-1}}$ $\mathrm{mol^{-1}}$ for $\mathrm{Sr_3U_{11}O_{36}}$(s) and $\mathrm{Sr_3U_2O_9}$(s), respectively. The uncertainties on the $C_\mathrm{p,m}^0(298.15\ \mathrm{K})$ values are within ±1%. Observed enthalpy increment data along with the fitted values (using Shomate's method [14]) for $\mathrm{Sr_3U_{11}O_{36}}$(s) and $\mathrm{Sr_3U_2O_9}$(s) are given in Tables 4 and 5, respectively. The $H^0(T) - H^0(298.15\ \mathrm{K})$ expressions for $\mathrm{Sr_3U_{11}O_{36}}$(s) and $\mathrm{Sr_3U_2O_9}$(s) are represented by the following equations:

$$
\begin{aligned}
&H^0(T) - H^0(298.15\ \mathrm{K})\ (\mathrm{J\ mol^{-1}}) \\
&\quad = -304\,152 + 962.72T\ (\mathrm{K}) + 177.63 \\
&\qquad \times 10^{-3}T^2\ (\mathrm{K}) + 3.954 \times 10^5/T\ (\mathrm{K}),
\end{aligned}
\tag{1}
$$

Table 2
Analysis of impurities present in for $Sr_3U_{11}O_{36}(s)$ and $Sr_3U_2O_9(s)$ by emission spectrometer

$Sr_3U_{11}O_{36}(s)$		$Sr_3U_2O_9(s)$	
Elements	ppm	Elements	ppm
Al	149	Al	113
B	<1	B	<1
Be	<1.1	Be	<1.1
Ca	156	Ca	54
Cd	105	Cd	<1.1
Co	<30	Co	<30
Cr	<154	Cr	<54
Cu	<21	Cu	<21
Fe	<141	Fe	112
Li	<21	Li	<21
Mg	<91	Mg	61
Na	37	Na	7
Mn	<21	Mn	21
Mo	36	Mo	<7
Ni	<54	Ni	54
Pb	<54	Pb	54
Si	3423	Si	1654
Sn	<12	Sn	<12
Ta	105	Ta	100
Ti	105	Ti	105
V	<54	V	<54
W	589	W	540
Zn	105	Zn	105
Ba	70	Ba	13

Table 3
Analysis of major components (Sr:U:O ratios) in $Sr_3U_{11}O_{36}(s)$ and $Sr_3U_2O_9(s)$ by XRF methods

Compounds	Methods	Sr/U	
		Expected	Observed
$Sr_3U_2O_9(s)$	XRF[a]	1.5	1.53
$Sr_3U_{11}O_{36}(s)$	XRF	0.2727	0.28

[a] XRF – X-ray fluorescence method.

$$H^0(T) - H^0(298.15\ \mathrm{K})\ (\mathrm{J\ mol^{-1}}) = -115\,817 + 319.18T\ (\mathrm{K}) + 58.01 \times 10^{-3}T^2\ (\mathrm{K}) + 46.201 \times 10^5/T\ (\mathrm{K}). \quad (2)$$

The first differential of Eqs. (1) and (2) gives the molar heat capacities for $Sr_3U_{11}O_{36}(s)$ and $Sr_3U_2O_9(s)$, respectively. The resulting equations are

$$C^0_{\mathrm{p,m}}(T)\ (\mathrm{J\ K^{-1}\ mol^{-1}}) = 962.72 + 355.26 \times 10^{-3}T\ (\mathrm{K}) - 3.954 \times 10^5/T^2\ (\mathrm{K}) \quad (3)$$

and

$$C^0_{\mathrm{p,m}}(T)\ (\mathrm{J\ K^{-1}\ mol^{-1}}) = 319.18 + 116.02 \times 10^{-3}T\ (\mathrm{K}) - 46.201 \times 10^5/T^2\ (\mathrm{K}). \quad (4)$$

$S^0_{\mathrm{m}}(298.15\ \mathrm{K})$ and $\Delta_f H^0_{\mathrm{m}}(298.15\ \mathrm{K})$ values are required for the computation of the thermodynamic functions for $Sr_3U_{11}O_{36}(s)$ and $Sr_3U_2O_9(s)$. Cordfunke et al. [8] have reported $\Delta_f H^0_{\mathrm{m}}(Sr_3U_{11}O_{36}(s),\ 298.15\ \mathrm{K})$ as −15905.6 kJ $\mathrm{mol^{-1}}$ from the solution calorimetric measurements. However, $\Delta_f H^0_{\mathrm{m}}(298.15\ \mathrm{K})$ for $Sr_3U_2O_9(s)$ and $S^0_{\mathrm{m}}(298.15\ \mathrm{K})$ for $Sr_3U_{11}O_{36}(s)$ and $Sr_3U_2O_9(s)$ are not reported.

Kubaschewski et al. [16] have compiled available estimation method for inorganic compounds and showed that missing thermochemical data can be estimated with reasonable accuracy. For the required compound the best choice of the estimation method is important. Mills's [17] had revised the method proposed by Latimer [18], in which the standard entropies of ionic compounds were obtained additively from values found empirically for the anionic and cationic constituents. Using Sr^{2+}, U^{4+} and O^{2-} data given by Mills's [17], standard entropy at 298.15 K for $Sr_3U_{11}O_{36}(s)$ and $Sr_3U_2O_9(s)$ have been calculated. The corresponding values are 1277.9 and 359.0 J $\mathrm{K^{-1}}$ $\mathrm{mol^{-1}}$, respectively.

The methods available for the estimation of $\Delta_f H^0_{\mathrm{m}}(298.15\ \mathrm{K})$ are often not very exact and apply to relatively small group of compounds. Thus, as many as possible methods should be used to estimate a single value, however, estimation method for higher uranates is not reported. Aronson [19] has suggested a method of estimation of heat of formation of mixed metal oxides based on Pauling's semiemprical equation [20]. The expression used for estimation is given as

$$\Delta_f H^0_{\mathrm{m}}(298.15\ \mathrm{K}) = -96.5 \sum \{x'(\mathrm{m}) - x'(\mathrm{O})\}^2, \quad (5)$$

where $x'(\mathrm{m})$ and $x'(\mathrm{O})$ are the pseudoelectronegativity of metals and Pauling's electronegativity of non-metal oxygen respectively. Aronson [18] has calculated the pseudoelectronegativity values for different metals and found it to be different from the Paulings values. Using the pseudoelectronegativity values he has estimated the enthalpy of formations for a number of compounds and obtained very good agreement between the experimental and calculated values, but in the case of uranium based compounds the results were not satisfactory. This might be due to different thermodynamic behavior of uranium compounds from other metal compounds. The pseseudoelectronegativity values for U^{+4}, Sr^{+2} and Ba^{+2} have been calculated in the present study by optimizing the agreement between experimental and calculated values of heat of formation of binary and ternary uranates. The corresponding values are 1.445, 1.06 and 1.059, respectively. Using these values enthalpy of formation values for ternary compounds in Sr–U–O, Ba–U–O and Ba–Sr–U–O systems have been calculated and compiled with the experimental value in Table 6. This shows that, the calculated and experimental values have excellent agreement. The $\Delta_f H^0_{\mathrm{m}}(Sr_3U_2O_9(s),\ 298.15\ \mathrm{K})$

Table 4
Experimental enthalpy increment values of $Sr_3U_{11}O_{36}(s)$

T (K)	$H^0(T) - H^0(298.15\text{ K})$ (J mol^{-1})			T (K)	$H^0(T) - H^0(298.15\text{ K})$ (J mol^{-1})		
	Experimental	Calculated	Δ% Error[a]		Experimental	Calculated	Δ% Error
299.0	905 ± 50	904.7	−0.03	573	305244 ± 1548	307198	0.64
301.0	3035 ± 905	3034.5	−0.19	598	334433 ± 1874	336208	0.53
332.8	27405 ± 827	27422	0.06	623.9	364523 ± 2269	366267	0.47
333.9	38217 ± 654	38289	0.19	673.1	423612 ± 1274	424922	0.31
343.8	48891 ± 1002	48977	0.18	722.3	484620 ± 1879	484443	−0.04
373.9	81375 ± 1122	81700	0.40	773.6	548745 ± 2701	547425	−0.24
376.0	83689 ± 1213	83995	0.37	824.2	613150 ± 690	610469	−0.44
423.9	136552 ± 1365	136797	0.18	s	680483 ± 1679	676336	0.61
473.1	190856 ± 1390	191905	0.55	949.0	775357 ± 4932	769863	0.71
523.1	246695 ± 1487	248810	0.86	1000.0	843620 ± 1051	836597	0.83
547.8	275186 ± 739	277253	0.64				

[a] Δ% Error = (fit value − measured value) × 100/fit value.

Table 5
Experimental enthalpy increment values of $Sr_3U_2O_9(s)$

T (K)	$H^0(T) - H^0(298.15\text{ K})$ (J mol^{-1})			T (K)	$H^0(T) - H^0(298.15\text{ K})$ (J mol^{-1})		
	Experiment	Calculated	Δ%Error[a]		Experimental	Calculated	Δ%Error
299.0	256.4 ± 50	256.7	0.12	580.7	96816 ± 2599	97049	0.24
301.0	861 ± 16	862	0.12	635.2	117472 ± 1795	117606	0.11
313.5	4724 ± 125	4685	−0.81	669.1	130489 ± 1456	130622	0.10
316.6	5699 ± 200	5644	−0.97	685.5	136885 ± 2689	136980	0.07
323.8	7991 ± 237	7885	−1.33	760.2	166392 ± 3656	166426	0.02
350.5	16615 ± 610	16365	−1.51	800.1	182472 ± 2757	182469	−0.01
426.0	41379 ± 905	41527	0.36	823.7	192195 ± 2610	192059	−0.07
463.6	54113 ± 135	54589	0.88	865.8	209667 ± 4322	209350	−0.15
483.2	61057 ± 819	61517	0.75	940.8	240980 ± 4521	240722	−0.11
514.0	72237 ± 1650	72556	0.44	974.2	255017 ± 3217	254925	−0.04
525.2	76336 ± 1320	76615	0.37	1000.0	265921 ± 4068	265992	0.03

[a] Δ%Error = (fit value − measured value) × 100/fit value.

Table 6
Comparison of calculated and experimental $\Delta_f H^0_m(298.15\text{ K})$ data[A]

Compounds	$\Delta_f H^0_m(298.15\text{ K})$ (kJ mol^{-1})		Δ%Error[B]
	Calculated	Experimental	
α-$SrUO_4(s)$	−1975.7	−1989.6	0.70
$Sr_2UO_5(s)$	−2607.5	−2635.6	1.07
$Sr_3UO_6(s)$	−3210.1	−3263.4	1.63
$Sr_2U_3O_{11}(s)$	−5247.7	−5242.9	−0.09
$SrU_4O_{13}(s)$	−5754.9	−5920.0[a]	–
$Sr_3U_2O_9(s)$	−4594.9	–	–
$Sr_3U_{11}O_{36}(s)$	−16026.1	−15905.6	−0.76
$UO_3(s)$	−1222.6	−1223.8[b]	0.10
$BaUO_4(s)$	−1976.7	−1993.8	0.86
$Ba_3UO_6(s)$	−3212.3	−3210.4	−0.06
$BaU_2O_7(s)$	−3261.1	−3237.2	−0.74
$Ba_{2.875}UO_{5.875}(s)$	−3137.8	–	–
$BaU_{6.24}O_{19.7}(s)$	−8509.6	–	–
$Ba_2U_3O_{11}(s)$	−5250.0	–	–
$Ba_2SrUO_6(s)$	−3211.6	−3257.3	1.4

[A] All the experimental values are taken from Ref. [19] except [a]estimated value [19] and [b]experimental value [20].

[B] Δ%Error = (experimental value − calculated value) × 100/experimental value.

Table 7
Thermodynamic functions for $Sr_3U_{11}O_{36}$(s)

T (K)	$C^0_{p,m}(T)$ (J K^{-1} mol^{-1})	$S^0_m(T)$ (J K^{-1} mol^{-1})	$-\{(G^0(T)-H^0(298.15\ K)\}/T$ (J K^{-1} mol^{-1})	$H^0(T)-H^0(298.15\ K)$ (J mol^{-1})	$\Delta_f H^0_m(T)$ (kJ mol^{-1})	$\Delta_f G^0_m(T)$ (kJ mol^{-1})
298.15	1064.2	1277.9	1277.9	0	−15905.6	−14984
300	1064.9	1284.5	1277.9	1.97	−15907.1	−14978
400	1102.4	1595.0	1320.1	110.3	−15998.5	−14655
500	1138.8	1845.9	1401.1	222.4	−15987.7	−14344
600	1174.8	2056.7	1493.3	338.1	−15978.0	−14040
700	1210.6	2240.5	1587.1	457.4	−15970.0	−13740
800	1246.3	2404.5	1679.2	580.2	−15640.4	−13442
900	1282.0	2553.3	1768.2	706.6	−15962.3	−13145
1000	1317.6	2690.3	1853.7	836.6	−15986.9	−12782
1100	1353.2	2817.5	1935.6	970.1	−16049.6	−12499
1200	1388.8	2936.8	2014.1	1107.2	−16033.5	−12194
1300	1424.3	3049.3	2089.4	1247.9	−16014.4	−11886
1400	1459.9	3158.1	2161.8	1392.1	−15992.2	−11574
1500	1495.4	3260.3	2231.6	1539.9	−16070.8	−11268

Table 8
Thermodynamic functions for $Sr_3U_2O_9$(s)

T (K)	$C^0_{p,m}(T)$ (J K^{-1} mol^{-1})	$S^0_m(T)$ (J K^{-1} mol^{-1})	$\{(G^0(T)-H^0(298.15\ K)\}/T$ (J K^{-1} mol^{-1})	$H^0(T)-H^\circ(298.15\ K)$ (J mol^{-1})	$\Delta_f H^0_m(T)$ (kJ mol^{-1})	$\Delta_f G^0_m(T)$ (kJ mol^{-1})
298.15	301.8	359.0	359.0	0	−4594.9	−4349.4
300	302.7	360.9	359.0	0.56	−4594.8	−4347.8
400	336.7	453.1	371.4	32.7	−4590.0	−4261.3
500	358.7	530.7	395.7	67.5	−4583.6	−4178.7
600	376.0	597.7	423.9	104.3	−4576.5	−4098.8
700	391.0	656.8	453.0	142.6	−4569.2	−4020.7
800	404.8	709.9	481.8	182.4	−4561.8	−3943.6
900	417.9	758.3	509.9	223.6	−4597.5	−3867.1
1000	430.6	803.0	537.0	266.0	−4553.1	−3779.6
1100	443.0	844.6	563.1	309.7	−4576.7	−3707.6
1200	455.2	883.7	588.2	354.6	−4566.2	−3632.0
1300	467.3	920.6	612.4	400.7	−4555.7	−3556.0
1400	479.2	955.7	635.7	448.0	−4544.1	−3479.4
1500	491.1	989.1	658.1	496.5	−4550.4	−3404.5

value: −4594.9 kJ mol^{-1}, calculated by this method could be reasonable.

Reliability of $\Delta_f H^0_m$($Sr_3U_2O_9$(s), 298.15 K) value can also be checked from temperature stability region of the solid. Phase diagram is required to find out the stability regions for different strontium uranates. Since experimental phase diagram is not available in the literature, it can be computed using thermodynamic data. SOLGASMIX-PV programme by Besmann [21], has been used to compute stability field for $Sr_3U_2O_9$(s). Calculations show that $Sr_3U_2O_9$(s) is stable in the Sr–U–O system if $\Delta_f H^0$($Sr_3U_2O_9$(s), 298.15 K) value is −4574± 40 kJ mol^{-1} at 800 K. This value was obtained with respect to $\Delta_f G^0(T)$ values of all the species present in the Sr–U–O system. Error in the $\Delta_f G^0(T)$ values (used for calculation) will reflect on the $\Delta_f H^0$($Sr_3U_2O_9$(s), 298.15 K) value. $Sr_3U_2O_9$(s) becomes unstable in Sr–U–O system at 800 K if $\Delta_f H^0$($Sr_3U_2O_9$(s), 298.15 K) value is taken less or more than −4574 ± 40 kJ mol^{-1}. However, $Sr_3U_2O_9$(s) has been found to be stable up to 1100 K. $\Delta_f H^0$($Sr_3U_2O_9$(s), 298.15 K) values calculated by two different methods agree well. In order to confirm an experimental value; at least more than one experimental measurement is required. Thus, estimated $\Delta_f H^0(Sr_3U_2O_9(s), 298.15\ K) = -4594.9\ kJ\ mol^{-1}$ value can be considered to be reasonable in the absence of any experimental value. $\Delta_f H^0_m(Sr_3U_2O_9(s), 298.15\ K) = -4594.9\ kJ\ mol^{-1}$ has been taken for the generation of the thermodynamic functions for $Sr_3U_2O_9$(s). Thermodynamic functions for $Sr_3U_{11}O_{36}$(s) and $Sr_3U_2O_9$(s) were computed and are given in Tables 7 and 8, respectively using selected $\Delta_f H^0_m(298.15\ \mathrm{K})$, $S^0_m(298.15\ \mathrm{K})$ values and entalpy increment values determined in this study and required data from literature [22–24].

4. Discussion

Enthalpy increment values for $Sr_3U_{11}O_{36}(s)$ and $Sr_3U_2O_9(s)$ have not been reported in the literature. $\Delta_f H^0_m(Sr_3U_{11}O_{36}(s), 298.15\ \mathrm{K})$ value ($-16026.1\ \mathrm{kJ\ mol^{-1}}$) calculated in this study agree reasonably well with the experimental value ($-15905.6\ \mathrm{kJ\ mol^{-1}}$) of Cordfunke et al. [8]. Thermodynamic functions for $Sr_3U_{11}O_{36}(s)$ and $Sr_3U_2O_9(s)$ have been computed for the first time.

Acknowledgements

Authors are also thankful to Dr M.D. Sastry, Head, Spectroscopy Section, Radiochemistry Division, BARC, for spectroscopic analysis, Mr N.D. Dahale for XRD analysis and Dr N.L. Mishra for XRF analysis.

References

[1] E.H.P. Cordfunke, B.O. Loopstra, J. Inorg. Nucl. Chem. 29 (1967) 51.
[2] B.O. Loopstra, H.M. Rietveld, Acta Crystallogr. B 25 (1969) 787.
[3] W.H. Zachariasen, Acta Crystallogr. 1 (1948) 281.
[4] J. Klima, O. Jakes, T. Moravec, J. Inorg. Nucl. Chem. 28 (1966) 1861.
[5] O.J. Sawyer, J. Inorg. Nucl. Chem. 34 (1972) 3268.
[6] JCPDS-ICDD Copyright(c), file no: 30-1312; Rev. Int. Hautes. Temp. Refract. 8 (1971) 37.
[7] H. Hoekstra, J. Katz, J. Am. Chem. Soc. 74 (1952) 1683.
[8] E.H.P. Cordfunke, P.V. Vlaanderen, M. Onink, D.J.W. Ijdo, J. Solid State Chem. 94 (1991) 12.
[9] E.H.P. Cordfunke, P.A.G. O'Hare, The Chemical Thermodynamics of Actinide Elements and Compounds, III, Miscellaneous Compounds, IAEA, Vienna, 1978, p. 51.
[10] E.F. Westrum Jr., H.A. Zainel, D. Jakes, in: Proceedings of the Symposium on Thermodynamics of Nuclear Materials, 1979, IAEA, Vienna, vol. II, 1980, p. 143.
[11] R. Saha, R. Babu, K. Nagarajan, C.K. Mathews, Thermochem. Acta 131 (1988) 183.
[12] J. Huang, M. Yamawaki, K. Yamaguchi, M. Yasumoto, H. Sakurai, Y. Susuki, J. Nucl. Mater. 247 (1997) 17.
[13] R. Prasad, R. Agarwal, K.N. Roy, V.S. Iyer, V. Venugopal, D.D. Sood, J. Nucl. Mater. 167 (1989) 261.
[14] C.H. Shomate, J. Phys. Chem. 58 (1954) 368.
[15] Z. Singh, S. Dash, R. Prasad, V. Venugopal, J. Alloys Comp. 279 (1998) 287.
[16] O. Kubaschewski, C.B. Alcock, P.J. Spencer, Materials Thermochemistry, 6th Ed., Pergamon, New York, 1993.
[17] K.C. Mills, National Physical Laboratory, DCS Note, 20 March 1974.
[18] W.E. Latimer, J. Am. Chem. Soc. 73 (1951) 1480.
[19] S. Aronson, J. Nucl. Mater. 107 (1982) 343.
[20] L. Pauling, The Nature of the Chemical Bond, 3rd Ed., Cornell University, 1960, p. 92.
[21] T.M. Besmann, Oak Ridge National Laboratory, Report ORNL-TM-5775 1977.
[22] H. Wanner, I. Forest (Eds.), Chemical Thermodynamics, vol-I, Chemical Thermodynamics of Uranium, 1992.
[23] E.H.P. Cordfunke, R.J.M. Konings (Eds.), Thermochemical Data for Reactor Materials and Fission Products, North-Holland, Amsterdam, 1990.
[24] M.W. Chase Jr., C.A. Davies, J.R. Downey Jr., D.J. Frurip, R.A. McDonald, A.N. Syverud, JANAF Thermochemical Tables, 3rd Ed., J. Phys. Chem. Ref. Data 14 1985.