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Thermochimica Acta 298 (1997) 59–64

thermochimica acta

Enthalpy increments of strontium and barium zirconates

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Received 26 August 1996; accepted 23 May 1997

Abstract

Enthalpy measurements on $SrZrO_3(s)$ and $BaZrO_3(s)$ were carried out using a Calvet micro-calorimeter. The increase in enthalpies with temperature were analyzed by least squares with the constraint that $H^0(T) - H^0$ (298.15 K) at 298.15 equals zero and C_p^0 (298.15 K) equals the literature value. The dependence of enthalpy on temperature was:

$$\underset{(SrZrO_3(s))}{H^0(T) - H^0(298.15\ \text{K})(\text{J/mol})} = 126.62T(\text{K}) + 5.478 \times 10^{-3}T^2(\text{K}) + 23.553 \times 10^5/T(\text{K}) - 46138$$

$$\underset{(BaZrO_3(s))}{H^0(T) - H^0(298.15\ \text{K})(\text{J/mol})} = 128.53T(\text{K}) + 2.571 \times 10^{-3}T^2(\text{K}) + 25.204 \times 10^5/T(\text{K}) - 47003$$

The first differential of the above equations with respect to temperature gave $C_p^0(T)$. Gibbs free energy functions were evaluated using $S^0(298.15)$ values from the literature. © 1997 Elsevier Science B.V.

Keywords: Enthalpy; Strontium; Barium; Zirconates

1. Introduction

Strontium and barium zirconates have been found to exist as separate oxide phases in irradiated mixed oxide fuel pellets of a fast breeder reactor [1]. High-temperature thermochemical properties of these compounds are required for evaluation of the interaction of chemical environment with fission products. Nagarajan et al. [3] have measured the enthalpy data for $SrZrO_3(s)$ and $BaZrO_3(s)$ by DSC in the temperature range 1030–1700 K. Levitskii et al. [4] have measured high-temperature enthalpies for the same compounds by drop calorimetry. Formichev et al. [5] have used drop calorimetry and measured enthalpies for $SrZrO_3(s)$ in the temperature range 562–2318 K. Cordfunke and Konings [6] have determined $H^0(T) - H^0$ (298.15 K) data for $BaZrO_3(s)$ between the temperature range 407–775 K using drop calorimetry. Cordfunke and Konings [7] have also reported enthalpy values for $SrZrO_3(s)$ and $BaZrO_3(s)$ in their compilations.

Recently, Gospodinov and Marchev [2] reported dependence of enthalpy data for $SrZrO_3(s)$ and $BaZrO_3(s)$ in the temperature range 298–500 K by differential scanning calorimeter (DSC). Their values are about six times greater than all the literature values [3–7]. With a view to resolve this discrepancy, a redetermination of the enthalpy data for strontium and barium zirconates has been carried out using a precise high-temperature Calvet calorimeter in the

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PII S0040-6031(97)00212-8

temperature range 384.8–991 K for $SrZrO_3$(s) and 365.7–991 K for $BaZrO_3$(s).

2. Experimental

$SrZrO_3$(s) and $BaZrO_3$(s) were prepared by heating equimolar proportions of their respective carbonates with ZrO_2(s) in an alumina boat at 1000 K for 200 h in dry air. The reaction was completed by repeated intermediate grinding and heating until the products were exclusively identified by X-ray diffraction analysis (XRD). Dried samples of $SrZrO_3$(s) and $BaZrO_3$(s) were made into pellets of 4 mm diameter and 1 mm thickness under a pressure of 100 MPa. These pellets were degassed under vacuum at 400 K and stored in a desiccator for $H^0(T) - H^0$ (298.15 K) measurements.

The Calvet calorimeter model HT-1000, supplied by Setaram of France, has been used for the change in enthalpy with temperature measurements of $SrZrO_3$(s) and $BaZrO_3$(s). The calorimeter was based on the heat-flow principle. The experimental assembly and procedure followed was reported in an earlier publication [8]. The calorimeter consisted of a massive fritted alumina block provided with two identical compartments surrounded by Pt to (Pt +10 mass% Rh) thermopiles which are connected in opposition to nullify the thermal disturbance during the experiments. Two identical closed alumina tubes, each with one end, were introduced into these compartments and the other ends of the tubes were connected to thermostat dropping mechanism where samples were maintained precisely at 298.15 K. The drop of the sample in the cell caused a change in the temperature of the cell which results in flow of heat from cell to the block or vice versa. This produces an electrical signal which is amplified by a nanovolt amplifier and integrated to obtain the enthalpy change. The acquisition and processing of signal was carried out by an on-line computer. The temperature of the sample was monitored by a calibrated platinum-resistance thermocouple (±0.1 K). To take measurements, a sample pellet of known mass was introduced into the sample dropping device and when the steady base line was achieved, sample was dropped into the calorimeter. At least three drop experiments were carried out for each isothermal temperature. Experiments were carried out in the temperature range at interval of around 30 K. The instrument was calibrated by Joule calibration [8] and the accuracy of the measurements were checked by dropping NBS alumina samples at the beginning and end of each experiment. The XRD patterns of $SrZrO_3$(s) and $BaZrO_3$(s) before and after the experiments remained the same.

3. Results

The $H^0(T) - H^0$ (298.15 K) values for $SrZrO_3$(s) and $BaZrO_3$(s) obtained at different temperatures are given in Tables 1 and 2, respectively. The data were fitted by least squares applying the following boundary conditions: C_p^0 (298.15 K) for $SrZrO_3$(s) and

Table 1
Experimental enthalpy increments of $SrZrO_3$(s)

T (K)	$H^0(T) - H^0$ (298.15 K) (J mol^{-1})			T (K)	$H^0(T) - H^0$ (298.15 K) (J mol^{-1})		
	Exp.	Cal.	Δ% Error		Exp.	Cal.	Δ% Error
384.8	9527	9516	−0.11	735.0	52513 ± 794	53091	1.10
427.0	14450 ± 340	14442	−0.05	775.9	57390	58439	1.83
457.8	18147 ± 454	18121	−0.14	837.3	65738 ± 908	66534	1.21
498.7	22910	23092	0.79	878.5	73223 ± 113	72005	−1.66
529.7	26653 ± 227	26915	0.99	909.2	77125 ± 226	76103	−1.32
601.5	36067 ± 680	35921	−0.40	929.6	78775 ± 907	78834	0.08
632.3	40377	39838	−1.33	950.1	82115	81586	−0.64
652.7	43326 ± 908	42448	−2.02	970.3	84178 ± 680	84305	0.15
683.5	46277 ± 680	46411	0.29	991.0	85972	87098	1.31
704.0	48997 ± 454	49062	0.13				

Table 2
Experimental enthalpy increments of $BaZrO_3$(s)

T (K)	$H^0(T) - H^0$ (298.15 K) (J mol^{-1})			T (K)	$H^0(T) - H^0$ (298.15 K) (J mol^{-1})		
	Exp.	Cal.	Δ% Error		Exp.	Cal.	Δ% Error
365.7	7280±276	7236	−0.60	775.9	57493	57519	0.05
408.6	12043±414	12112	0.57	806.8	61617 ± 276	61492	−0.20
427.0	14218±553	14250	0.23	837.3	65353 ± 1242	65427	0.11
457.8	17842±691	17882	0.22	868.2	69516 ± 1104	69427	−0.13
498.7	22739±829	22788	0.22	878.2	70897 ± 138	70724	−0.24
529.3	26562±829	26509	−0.19	909.3	74828 ± 276	74766	−0.08
544.9	28335±553	28421	0.31	929.6	77305 ± 415	77411	0.14
601.5	35471±691	35427	−0.12	950.1	80081	80086	0.01
632.3	39270±967	39280	0.03	970.3	82621 ± 276	82727	0.13
704.0	48389±967	48336	−0.11	981.0	83990 ± 691	84128	0.16
735.0	52439±276	52284	−0.29				

$BaZrO_3$(s) are 103.39 [9] and 101.71 J mol^{-1} K^{-1} [9], respectively, and $H^0(T) - H^0(298.15\text{ K}) = 0$ at 298.15 K. The increase in enthalpy with temperature for $SrZrO_3$(s) and $BaZrO_3$(s) are, respectively, represented by the following polynomial equations:

$$H^0(T) - H^0(298.15\text{ K})(\text{J/mol}) = 126.62T(\text{K}) + 5.478 \times 10^{-3}T^2(\text{K}) + 23.553 \times 10^5/T(\text{K}) - 46138 \quad (1)$$

$$H^0(T) - H^0(298.15\text{ K})(\text{J/mol}) = 128.53\,T(\text{K}) + 2.571 \times 10^{-3}T^2(\text{K}) + 25.204 \times 10^5/T(\text{K}) - 47003 \quad (2)$$

The molar heat capacity is the first differential of $H^0(T) - H^0$ (298.15 K) with respect to temperature. The values for $SrZrO_3$(s) and $BaZrO_3$(s) are, respectively, given by the following equations:

$$C^0_\text{p}(T)(\text{J/mol K}) = 126.62 + 10.956 \times 10^{-3}T^2(\text{K}) - 23.553 \times 10^5/T^2(\text{K}) \quad (3)$$

$$C^0_\text{p}(T)(\text{J/mol K}) = 128.53 + 5.142 \times 10^{-3}T^2(\text{K}) - 25.204 \times 10^5/T^2(\text{K}) \quad (4)$$

Other thermodynamic parameters were calculated using $S^0(298.15) = 115.1$ J mol^{-1} K^{-1} for $SrZrO_3$(s) and $S^0(298.15) = 124.7$ J mol^{-1} K^{-1} for $BaZrO_3$(s) [9].

4. Discussion

The increase in enthalpy for $SrZrO_3$(s) and $BaZrO_3$(s) with temperature from the present study are compared with the literature in Tables 3 and 4,

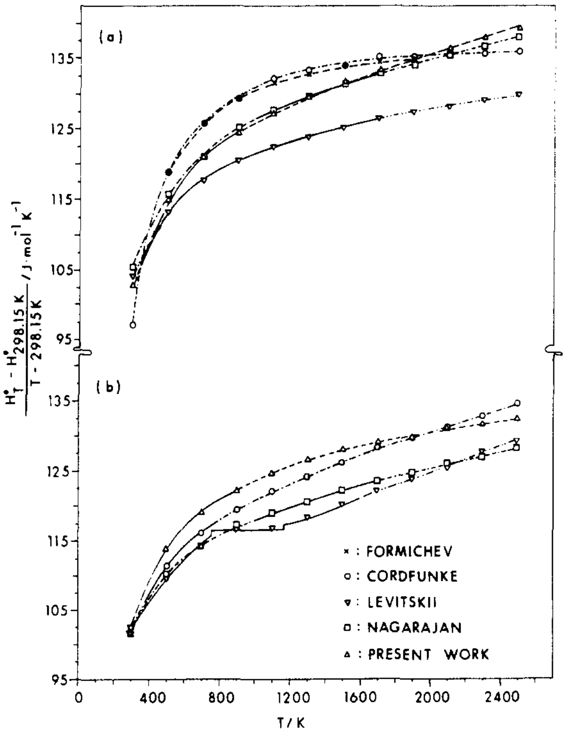

Fig. 1. The reduced enthalpy increment of (a) $SrZrO_3$ and (b) $BaZrO_3$ as a function of temperature. Bold line indicates experimental temperature range and dotted line represents intrapolated and extrapolated values.

Table 3
Comparison of enthalpy increment data of $SrZrO_3$(s)

Authors	Method	Temp. range (K)	$H^0(T) - H^0$ (298.15 K) (J mol^{-1})				$H^0(T) - H^0$ (298.15 K)	
			AT (K)	$B \times 10^3 T^2$ (K)	$C \times 10^{-5}/T$ (K)	D	500 K (kJ mol^{-1})	1500 K (kJ mol^{-1})
Formichev et al. [5]	DC [c]	562–2318	147.07	−2.08	41.48	−57277	24.04	161.42
Levitskii et al. [4]	DC [c]	298–1620	124.64	2.93	20.46	−44283	22.86	150.63
Cordfunke and Konings [7]	C [a]	—	143.91	−1.16	35.44	−54703	23.55	160.92
Nagarajan et al. [3]	DSC [b]	1030–1694	128.92	4.42	25.03	−47222	23.35	157.78
Gospodinov and Marchev [2]	DSC [b]	298–500	—	—	—	—	177.12	—
Present study	DC [c]	384–991	126.62	5.48	23.55	−46138	23.25	157.69

[a] C – Compilation.
[b] DSC – Differential Scanning Calorimeter.
[c] DC – Drop Calorimetery.

Table 4
Comparison of enthalpy increment data of $BaZrO_3$(s)

Authors	Method	Temp. range (K)	$H^0(T) - H^0$ (298.15 K) (J mol^{-1})				$H^0(T) - H^0$ (298.15 K)	
			AT (K)	$B \times 10^3 T^2$ (K)	$C \times 10^{-5}/T$ (K)	D	500 K (kJ mol^{-1})	1500 K (kJ mol^{-1})
Levitskii et al. [4]	DC [b]	298–758	107.24	13.05	11.80	−37091	22.15	153.91
		758–1175	116.19	0.37	—	−34610	23.58	140.52
		1175–1606	103.55	9.24	—	−31698	22.39	144.21
Cordfunke and DC Konings [6]	DC [b]	407–775	117.76	4.49	16.65	−41094	22.47	151.58
Nagarajan et al. [3]	DSC [a]	1030–1687	118.11	6.71	18.14	−41895	22.24	146.77
Gospodinov and Marchev [2]	DSC [a]	298–500	—	—	—	—	120.92	—
Present study		365–981	128.53	2.57	25.20	−47003	22.95	153.26

[a] DSC – Differential Scanning Calorimeter.
[b] DC – Drop Calorimetery.

respectively. A comparison of reduced enthalpy function versus temperature is shown in Fig. 1 in the temperature range 300–2500 K for all the reported data. Data for all the reported work were extrapolated to cover the entire temperature range using the experimentally obtained enthalpy increment fit obtained in the experimental temperature range.

From Fig. 1 it is clear that enthalpy values for $SrZrO_3$(s) reported by Levitskii et al. [4] are considerably lower than all other reported values. Our values match excellently with those of Nagarajan et al. [3] in the temperature range 300–2500 K but are lower than those of Cordfunke's [6] and Formiichev's [5] by about 4.2%. The extrapolated values of Formichev et al. [5] are around 4.2% higher in the range 300–1900 K and about 2.5% lower at 2500 K than the present data. It is seen from Table 3 that $H^0(T) - H^0$ (298.15 K) values for $SrZrO_3$(s) agree very well with that of Nagarajan et al. [3] in the temperature range 298.15–1500 K. Values of Gospodinov and Marchev [2] are about 650% higher than our data. Accuracy of their results is difficult to judge as they did not report the reference material data. As we have measured the enthalpy increment data by a more precise calorimeter than DSC and after each measurement values were checked by NBS standard, thus such

Table 5
Thermodynamic functions of $SrZrO_3(s)$

T (K)	$H^0(T) - H^0(298.15)$ (J mol^{-1})	C^0_p (J mol^{-1} K^{-1})	$S^0(T)$ (J mol^{-1} K^{-1})	fef [a] (J mol^{-1})
300	192.0	103.7	115.7	115.1
350	5579.5	111.2	132.3	116.4
400	11274.7	116.3	147.5	119.3
450	17184.3	119.9	161.4	123.3
500	23252.1	122.7	174.2	127.7
550	29442.5	124.9	186.0	132.5
600	35731.6	126.7	196.9	137.4
650	42103.0	128.2	207.2	142.4
700	48544.9	129.5	216.7	147.3
750	55048.8	130.7	225.7	152.3
800	61608.1	131.7	234.2	157.1
850	68217.8	132.7	242.2	161.9
900	74874.2	133.6	249.8	166.6
950	81574.2	134.6	257.1	171.2
1000	88315.3	135.2	263.9	175.6

[a] fef= $-(G^0(T) - H^0(298.15))/T$

Table 6
Thermodynamic functions of $BaZrO_3(s)$

T/K	$H^0(T) - H^0(0298.15)$ (J mol^{-1})	C^0_p (J mol^{-1} K^{-1})	$S^0(T)$ (J mol^{-1} K^{-1})	fef [a] (J mol^{-1})
300	188.7	102.1	125.3	124.7
350	5498.6	109.8	141.7	125.9
400	11121.3	114.8	156.7	128.9
450	16956.9	118.4	170.4	132.8
500	22945.5	121.0	183.1	137.2
550	29048.7	123.0	194.7	141.9
600	35241.2	124.6	205.5	146.7
650	41505.2	125.9	215.5	151.6
700	47828.3	126.9	224.9	156.5
750	54201.1	127.9	233.7	161.3
800	60616.8	128.7	241.9	166.1
850	67070.1	129.4	249.8	170.9
900	73556.8	130.1	257.2	175.5
950	80073.7	130.6	264.2	179.9
1000	86618.2	131.2	270.9	184.3

[a] fef=$-(G^0(T) - H^0(298.15))/T$.

a high value reported by Gospodinov and Marchev [2] might involve some error. Table 5 gives the derived thermodynamic functions for $SrZrO_3(s)$ which were calculated using $S^0(298.15) = 115.1$ J mol^{-1} K^{-1} [9].

In the case of $BaZrO_3(s)$, as seen in Fig. 1(b), our data are about 4.4% higher than that of Nagarajan et al. [3] in the temperature range 300–2500 K. Our values are 2.4% more as compared to Cordfunke's in the experimental temperature range. Our extrapolated values are around 1.6% lower than that of Cordfunke's. Reduced enthalpy functions calculated from the data given by other authors [2,3,6], except Levitskii [4] show a smooth curve. No polymorphic transitions were observed in the present study. Table 4 shows that our data on $BaZrO_3(s)$ and that of Cordfunke and

Konings [6] covered the same temperature range but our values are about 2.5% higher than that of Cordfunke and Konings [6] and the extrapolated values above 2100 K are about 1.6% lower. The values of Levitskii et al. [4] and Nagarajan et al. [3] are, respectively, about 6.2 and 4.4% lower than the present values in the entire temperature range. Gospodinov and Marchev [2] data are unreasonably higher than all the values. Because of the same reason given for $SrZrO_3(s)$, the data of Gospodinov and Marchev [2] has not been considered for comparison. Table 6 gives the thermodynamic functions of $BaZrO_3(s)$, which were calculated using $S^0(298.15) = 124.7\ J\ mol^{-1}\ K^{-1}$ [9].

Acknowledgements

Authors are thankful to Dr. H.C. Jain, Head, Fuel Chemistry Division, for his constant encouragement during the progress of this work. Authors are also thankful to Dr. K.D. Singh for X-ray diffraction analysis.

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