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ENTHALPY INCREMENTS OF BARIUM ZIRCONATE, $BaZrO_3$, AND AN ASSESSMENT OF ITS THERMOCHEMICAL PROPERTIES

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ABSTRACT

The enthalpy increments of barium zirconate ($BaZrO_3$) were measured with a drop calorimeter between 407 and 775 K. From these measurements, and high-temperature X-ray diffraction analysis, it is concluded that $BaZrO_3$ has no phase transitions up to 1375 K. From an assessment of the available literature, the thermochemical properties of $BaZrO_3$ were derived.

INTRODUCTION

Barium zirconate ($BaZrO_3$) is an interesting compound, not only because of its application in the electroceramic industry, but also because it is formed in fuel pins of nuclear reactors under the conditions of temperature and oxygen potential during normal operation [1].

The high-temperature thermochemical properties are needed for the evaluation of the fuel-fission product interactions in nuclear reactors. In this paper, we report the high-temperature enthalpy increment measurements of $BaZrO_3$ by drop calorimetry as well as a critical assessment of its enthalpy of formation. The data enable us to evaluate the thermodynamic properties of $BaZrO_3$ up to 1500 K.

EXPERIMENTAL

The $BaZrO_3$ sample was prepared by the reaction in the solid state of $BaCO_3$ and ZrO_2 at about 1700 K. $BaCO_3$ (Cerac, p.a.) was dried before use at 500 K; ZrO_2 was prepared by heating zirconyl nitrate in oxygen to 1200 K, and keeping it at this temperature for 15 h.

Stoichiometric amounts of $BaCO_3$ and ZrO_2 were thoroughly mixed, and then pressed into a pellet which was first heated in oxygen in a gold boat at 1200 K. The reaction was completed by heating the pellet in a TaC crucible

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in a high-frequency furnace at 1700 K for several hours; this heating was carried out in an argon atmosphere. The resulting compound was pale green in colour; X-ray diffraction analysis showed it to be phase pure: only the reflections of the $BaZrO_3$ perowskite-type structure were present. A scanning electron microscopic analysis showed no other elements to be present. High-temperature X-ray patterns were recorded in purified oxygen up to 1375 K with an Enraf–Nonius high-temperature Guinier camera.

The isothermal diphenyl ether drop calorimeter, in which the enthalpy increments were measured, has been previously described by Cordfunke et al. [2]. Briefly, the sample is enclosed in a spherical vitreous silica ampoule which has a volume of 4.2 cm^3. The ampoule is heated in a furnace whose temperature is measured to ± 0.1 K with a Pt–(Pt + 10 mass% Rh) thermocouple. After thermal equilibration, the ampoule is dropped into the calorimeter. The energy of the ampoule plus the sample now melts solid diphenyl ether in equilibrium with its liquid in a closed system. The resulting volume increase of the ether is determined by weighing the displaced mercury. The ratio of heat input to mass of mercury making up the volume change is a constant for the apparatus (79.977 ± 0.063) J g^{-1}, and is obtained by calibration with α-SiO_2 and compared with the National Bureau of Standards (NBS) standard reference material (No. 720) synthetic sapphire, Al_2O_3. Our results with sapphire all agree within 0.2% with the data given by NBS. The enthalpy contributions of the vitreous silica were determined separately.

For the present study, 8.86008 g of $BaZrO_3$ was sealed in the ampoule, which had an empty weight of 1.27392 g. A correction on the measurements was made for the difference in enthalpy between the final calorimeter temperature and the standard reference temperature, 298.15 K, using $C_p^\ominus(298.15\ \mathrm{K}) = 101.71$ J mol^{-1} K^{-1} [3].

RESULTS

The high-temperature enthalpy increments of $BaZrO_3$

The results of the drop calorimetric measurements, listed in Table 1, can be represented by the polynomial equation

$$\{H^\ominus(T) - H^\ominus(298.15\ \mathrm{K})\}(\mathrm{J\ mol^{-1}})$$
$$= 118.112[T(\mathrm{K})] + 6.7099 \times 10^{-3}[T(\mathrm{K})]^2$$
$$+ 18.1369 \times 10^5[T(\mathrm{K})]^{-1} - 41894.7$$

for the temperature interval 298.15–775 K, applying as boundary conditions, $C_p^\ominus(298.15\ \mathrm{K}) = 101.71$ J mol^{-1} K^{-1} [3] and $\{H^\ominus(T) - H^\ominus(298.15\ \mathrm{K})\} = 0$ at 298.15 K. The standard deviation is 0.30%.

TABLE 1

Experimental enthalpy increments of $BaZrO_3$

T (K)	$\{H^\ominus(T) - H^\ominus(298.15\ K)\}$ (J mol^{-1})		Δ (%)
	exp.	calc.	
406.7	11787	11711	0.65
421.9	13471	13430	0.31
439.1	15373	15392	−0.12
457.1	17550	17464	0.49
460.4	17798	17846	−0.27
479.5	20098	20065	0.16
504.4	22913	22984	−0.31
524.3	25318	25335	−0.07
549.2	28318	28299	0.07
575.3	31567	31428	0.44
604.4	34910	34944	−0.10
625.4	37583	37497	0.23
651.2	40471	40650	−0.44
654.0	41061	40994	0.16
683.0	44435	44561	−0.28
704.2	47252	47183	0.15
724.1	49526	49653	−0.26
739.4	51448	51559	−0.22
751.5	53140	53069	0.13
763.0	54631	54508	0.23
774.6	55995	55962	0.06

An assessment of the enthalpy of formation at 298.15 K

The enthalpy of formation of $BaZrO_3$ at 298.15 K has been derived from four different types of measurements:

(a) L'vova and Feodos'ev [4] measured the enthalpy of reaction of stoichiometric amounts of $BaCO_3$ and ZrO_2 in a calorimetric bomb, carbon black being used as the initiating substance. After the experiments, the amount of unreacted ZrO_2 was determined, and corrections for unreacted mixture and combustion of carbon black were made. For the enthalpy of the reaction

$$BaCO_3(s) + ZrO_2(s) = BaZrO_3(s) + CO_2(g)$$

(after a pV correction) the value $\Delta H^\ominus(298.15\ K) = +(143.93 \pm 1.7)$ kJ mol^{-1} has been found. If we combine this value with the enthalpies of formation of $BaCO_3$ [5], ZrO_2 [6] and CO_2 [7], we obtain for $BaZrO_3$, $\Delta_f H^\ominus(298.15\ K) = -(1779.2 \pm 2.0)$ kJ mol^{-1}.

(b) Odoj and Hilpert [8] measured the BaO pressure of the equilibrium

$$BaZrO_3(s) = ZrO_2(s) + BaO(g)$$

in a mass spectrometer in combination with a Knudsen cell. The 'third-law' enthalpy of dissocation of this equilibrium at 298.15 K has been recalculated by us from the experimental BaO pressures, using the free energy functions of $BaZrO_3$ (as derived in this paper), ZrO_2 [6] and BaO(g) [6]. From the two sets of measurements, we derive $\Delta H^\ominus = (466.4 \pm 2.2)$ kJ mol^{-1} and $\Delta H^\ominus = (465.0 \pm 2.6)$ kJ mol^{-1}, respectively; we take $\Delta H^\ominus(298.15\ K) = (466.0 \pm 1.7)$ kJ mol^{-1} as the weighted mean. By combining this value with the enthalpies of formation of ZrO_2 [6] and BaO(g) [9], we obtain for $BaZrO_3$: $\Delta_f H^\ominus(298.15\ K) = -(1694.0 \pm 7.5)$ kJ mol^{-1}.

(c) Levitskii et al. [10] calculated the enthalpy of formation of $BaZrO_3$ from EMF measurements with different types of electrochemical cells. However, because of reactions at the electrodes in cell types I and II, only cell type III

$$-O_2,Pt|CaO,BaF_2,ZrO_2|CaF_2|BaZrO_3,CaF_2|Pt,O_2$$

with the overall reaction

$$CaO(s) + BaF_2(s) + ZrO_2(s) = BaZrO_3(s) + CaF_2(s)$$

will be considered here. When the measured EMF values are recalculated by 'third-law' analysis, using the free energy functions of CaO(s) [11], BaF_2 and CaF_2 [12], ZrO_2(s) [6] and $BaZrO_3$ (this work), we obtain for the overall electrode reaction: $\Delta H^\ominus(298.15\ K) = -(54.99 \pm 0.62)$ kJ mol^{-1}. Combining this value with auxiliary data for the enthalpies of formation at 298.15 K of CaO(s) and CaF_2(s) [11], ZrO_2 [6] and BaF_2(s), $-(1203.0 \pm 2.0)$ kJ mol^{-1} [13], we obtain for the enthalpy of formation of $BaZrO_3$: $\Delta_f H^\ominus(298.15\ K) = -(1765.4 \pm 3.1)$ kJ mol^{-1}.

(d) Takayama-Muromachi and Navrotsky [14] determined the enthalpy of solution of $BaZrO_3$(s) in a $LiBO_2$–$NaBO_2$ solvent at 1068 K. By combining this value with the enthalpies of solution of BaO and ZrO_2, as determined under the same conditions, they obtained for the enthalpy of formation of $BaZrO_3$(s) from the oxides the value $\Delta_f H^\ominus(1068\ K) = -(123.9 \pm 4.1)$ kJ mol^{-1}, and, using the enthalpy increments of BaO(s) and ZrO_2(s) [15] and

TABLE 2

The enthalpy of formation of $BaZrO_3$ at 298.15 K

Author	Method [a]	$\Delta_f H^\ominus$ (kJ mol^{-1})
L'vova and Feodos'ev (1964) [4]	C	-1779.2 ± 2.0
Odoj and Hilpert (1976) [8]	M	-1694.0 ± 7.5
Levitskii et al. (1974) [10]	E	-1765.4 ± 3.1
Takayama-Muromachi and Navrotsky (1988) [14]	S	-1771.4 ± 4.9
Selected value:		-1774.8 ± 5.0

[a] C, Combustion calorimetry; M, mass spectrometry; E, EMF; S, solution calorimetry.

$BaZrO_3(s)$ from this study, $\Delta_f H^\ominus$ (298.15 K) = $-(122.9 \pm 4.5)$ kJ mol^{-1}. When this value is combined with the enthalpies of formation of BaO(s) [15] and $ZrO_2(s)$ [6] at 298.15 K, we obtain for the enthalpy of formation of $BaZrO_3$ the value: $\Delta_f H^\ominus$(298.15 K) = $-(1771.4 \pm 4.9)$ kJ mol^{-1}.

From the four sets of measurements (Table 2), we select $\Delta_f H^\ominus$(298.15 K) = $-(1774.8 \pm 5.0)$ kJ mol^{-1}, being the weighted mean of the measurements (a), (c) and (d), the uncertainty being raised to 0.3%.

DISCUSSION

The results of the enthalpy increment measurements are represented graphically in Fig. 1 in a $\{H^\ominus(T) - H^\ominus(298.15\ \mathrm{K})\}/(T - 298.15)$ versus T plot together with the low-temperature data of King and Weller [3], the high-temperature drop calorimetric measurements by Levitskii et al. [16] from 377 to 1606 K, and the high-temperature data by Nagarajan et al. [17] from 1030 to 1687 K.

Our data join smoothly with the low-temperature data in the 298.15 K region, but are considerably higher than the results of Levitskii et al. [16] and Nagarajan et al. [17]. The results of the former authors are probably in error as they report two polymorphic transitions, at 758 and 1175 K, which were not observed in the present measurements. In addition, we carried out high-temperature X-ray diffraction which confirmed that the crystal structure of $BaZrO_3$ remains unchanged up to 1375 K.

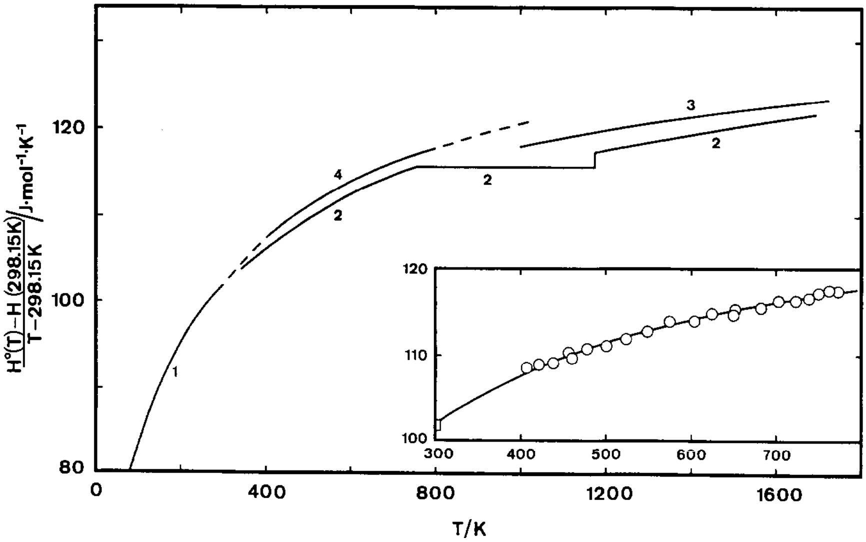

Fig. 1. The reduced enthalpy increment of $BaZrO_3$ as a function of the temperature. The inset gives details of the present measurements symbols: 1, King and Weller [3]; 2, Levitskii et al. [16]; 3, Nagarajan et al. [17]; 4, present results.

TABLE 3

Thermodynamic functions of $BaZrO_3(s)$

T (K)	$C_p^\ominus$ (J mol^{-1} K^{-1})	$S^\ominus$ (J mol^{-1} K^{-1})	$-(G^\ominus - H^\ominus(298.15))/T$ (J mol^{-1} K^{-1})	$H^\ominus - H^\ominus(298.15)$ (J mol^{-1})	$\Delta_f H^\ominus$ (J mol^{-1})	$\Delta_f G^\ominus$ (J mol^{-1})
298.15	101.710	124.700	124.700	0	−1774800	−1690065
300	101.986	125.330	124.702	188	−1774794	−1689540
400	112.144	156.242	128.848	10958	−1774386	−1661177
500	117.567	181.900	136.968	22466	−1773990	−1632927
600	121.126	203.668	146.316	34411	−1773680	−1604746
700	123.804	222.549	155.888	46662	−1773470	−1576608
800	126.014	239.228	165.283	59156	−1773353	−1548493
900	127.951	254.185	174.344	71856	−1773317	−1520388
1000	129.718	267.758	183.017	84741	−1773347	−1492283
1100	131.375	280.200	191.294	97796	−1780065	−1463485
1200	132.956	291.699	199.188	111013	−1783320	−1434518
1300	134.484	302.402	206.721	124386	−1782129	−1405496
1400	135.974	312.423	213.917	137909	−1780845	−1376571
1500	137.436	321.855	220.802	151580	−1779476	−1347745
1600	138.875	330.771	227.398	165395	−1778021	−1319009
1700	140.298	339.233	233.730	179354	−1776499	−1290366
1800	141.708	347.292	239.817	193454	−1774916	−1261815
1900	143.107	354.991	245.678	207695	−1773286	−1233356
2000	144.498	362.367	251.329	222076	−1771619	−1204981

There is no overlap of the present results with the data of Nagarajan et al. [17], but the situation is quite similar to that of $SrZrO_3$ where the data of Nagarajan et al. (as well as of Levitskii et al. [16]) are also significantly lower than the drop calorimetric results of Fomichev et al. [18], which are in excellent agreement with the low-temperature data of King and Weller [3] for this compound. This suggests that the results of the calorimetric method of Nagarajan et al. [17] are less reliable. The accuracy of their measurements is difficult to judge as they did not report reference material data.

Table 3 gives the molar thermodynamic functions of $BaZrO_3$, calculated from the present enthalpy increments, the assessed value for the enthalpy of formation and the entropy, $S^{\ominus}(298.15 \text{ K}) = (124.7 \pm 1.2)$ J mol^{-1} K^{-1}, as reported by King and Weller [3]

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