Heat capacity measurements on $BaThO_3$ and $BaCeO_3$

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Abstract

Heat capacity measurements of $BaThO_3$ and $BaCeO_3$ were carried out using differential scanning calorimetry in the temperature range 320–820 K. From the heat capacity values of $BaThO_3$ and $BaCeO_3$, other thermodynamic functions such as enthalpy increments, entropies and Gibbs energy functions of these compounds were derived. © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

Thoria rich $(Th,U)O_2$ and $(Th,Pu)O_2$ are candidate fuels for future nuclear reactors. The chemical interaction of the alkaline earth fission product barium with the thoria matrix could result in the formation of $BaThO_3$ which will influence the properties of the fuel [1]. Similarly, the interactions of barium with cerium, an important fission product, could lead to the formation of $BaCeO_3$ which could also be formed in (U, Pu) mixed oxide fuels. Hence to understand the chemical state of barium in the irradiated fuels, thermodynamic data on $BaThO_3$ and $BaCeO_3$ are necessary. In the literature, studies on the Gibbs energy of formation and thermal expansion of $BaThO_3$ above room temperature only have been reported [2,3]. There are no data for the heat capacity of this compound. For $BaCeO_3$ the only data reported in the literature are the enthalpy increment values of Saha et al. [4] who have employed drop calorimetry in the temperature range 1000–1700 K. There are no heat capacity or enthalpy data for lower temperatures. Hence in this study, heat capacity measurements on $BaThO_3$ and $BaCeO_3$ in the temperature range 320–820 K were carried out using differential scanning calorimetry. In order to standardize the procedure for the heat capacity measure-

ments by DSC, heat capacity measurements on ThO_2, whose heat capacity data are well established, were also carried out. The results are presented and discussed in this paper.

2. Experimental

2.1. Sample preparation

ThO_2 of 99.99% purity (M/s. BDH Chemicals), CeO_2 of 99.9% purity supplied by M/s. Indian Rare Earths and AR grade $BaCO_3$ (M/s. Sarabhai Chemicals, India) were used for preparing the samples. $BaThO_3$ was prepared by combustion synthesis using citric acid and barium nitrate supplied by Merck and thorium nitrate supplied by Indian Rare Earths. Citric acid was used as the fuel for combustion and was added to a mixture of barium nitrate and thorium nitrate solutions, and the solution was heated on a hot plate at 573 K. The resultant porous product was then heated at 1173 K in a furnace to eliminate carbon and hydrogen as CO_2 and H_2O. The product obtained was then pelletized and heated at 1473 K for 12 h. The pellet was ground, pelletized and heated further at 1673 K for 60 h. The resultant product was single-phase $BaThO_3$ ($a = 634.88$ pm, $b = 638.73$ pm, $c = 899.5$ pm), as confirmed using the X-ray diffraction pattern [5]. For the preparation of $BaCeO_3$, stoichiometric amounts of $BaCO_3$ and CeO_2 were thoroughly mixed and pressed into pellets which were heated at 973 K for 8 h, and again heated at 1373 K for 12 h. The resultant product was characterized using

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X-ray diffraction to be single-phase BaCeO$_3$ ($a = 879.5$ pm, $b = 626.2$ pm, $c = 623.3$ pm) by comparing with the pattern given in the JCPDS file.

2.2. Equipment

A heat flux type differential scanning calorimeter, model number DSC821e/700 of M/s. Mettler Toledo GmbH, Switzerland was used in this study.

2.3. Calorimetric measurements

The samples for DSC measurements were pelletized and hermetically sealed in 40 µl Al-pans. High purity argon gas was used as the purge gas in these measurements. DSC measurements on all the samples were carried out in the temperature range 320–820 K using a heating rate of 10 K min^{-1} and a purge gas flow rate of 50 ml min^{-1}. A disc of sapphire was used as the heat capacity standard. The amount of sample taken was determined by the trial and error method so that the heat flows of the sample nearly matched with that of the sapphire disc. The amount of the sample used varied from 20 to 100 mg. Initial experiments on BaThO$_3$ revealed that it is slightly hygroscopic in nature. The sample was found to lose weight during heating indicating that the sample contained moisture. Therefore, BaThO$_3$ samples were heated to 823 K in the DSC cell for two hours before the heat capacity measurements for removing the moisture. The weight of the sample determined after the completion of the measurements was used for the computation of the heat capacity. A three-segment heating programme was used in these measurements. The first segment lasting for five minutes was an isothermal segment at the initial temperature; the second segment was a dynamic segment with a heating rate of 10 K min^{-1} and the final segment lasting for 5 min was another isothermal segment at the final temperature.

3. Results and discussion

The heat capacity data of sapphire given by National Institute of Standards and Technology, USA (NIST) was used for computing the heat capacities of the samples. The heat capacity data of ThO$_2$ measured by DSC in the present work and given in Table 1 are the mean values of five or six measurements and the relative standard deviations are in the range 1–2%. The heat capacity data of ThO$_2$ from the recent evaluation of Bakker et al. [6] are also given in Table 1. The measured heat capacity values of ThO$_2$ were fitted to the following polynomial in temperature by the least-squares method.

Table 1
Heat capacity data of ThO$_2$

Temp. (K)	C_p (J K^{-1} mol^{-1})		
	Measured	Fit	Literature [6]
298.15	–	58.4	61.8
300	–	58.6	61.9
400	66.9	67.3	67.6
500	70.8	71.4	71.2
600	73.2	73.7	73.9
700	75.5	75.2	75.8
800	75.7	76.2	77.2

C_p (J K^{-1} mol^{-1})

$$= 77.8006 + 1.41 \times 10^{-3} \cdot T - 1.764343 \times 10^6 \cdot T^{-2}$$

$$(320\text{–}820 \text{ K}). \tag{1}$$

The standard error of the fit is 0.54. The measured data along with the fit values are shown in Fig. 1. The assessed data of Bakker et al. [6] are also shown in Fig. 1. As can be seen, the present data are in very good agreement with those of Bakker et al. [6] within ±2%.

The heat capacity data of BaThO$_3$ measured by DSC and shown in Table 2 are the mean of 5 or 6 measurements whose relative standard deviations are in the range 1–2%. The measured heat capacity values of BaThO$_3$ were fitted to the following expression using the least-squares method.

C_p (J K^{-1} mol^{-1})

$$= 137.9046 + 5.272 \times 10^{-2} \cdot T - 2.432487 \times 10^6 \cdot T^{-2}$$

$$(320\text{–}820 \text{ K}). \tag{2}$$

The standard error of the fit is 0.69. The measured values are shown in Fig. 2 along with the values from the fit equation. There are no heat capacity data reported in
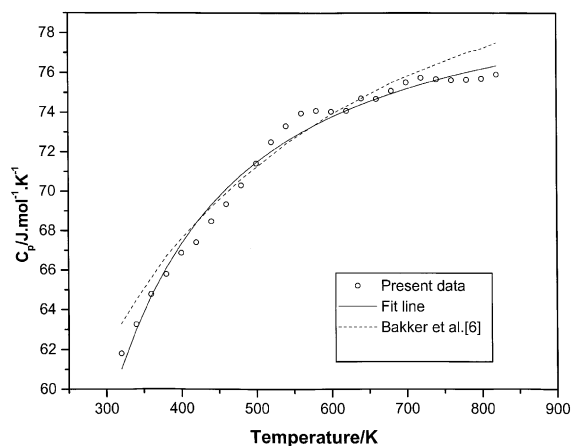

Fig. 1. Heat capacity data of ThO$_2$.

Table 2
Thermodynamic functions of BaThO$_3$

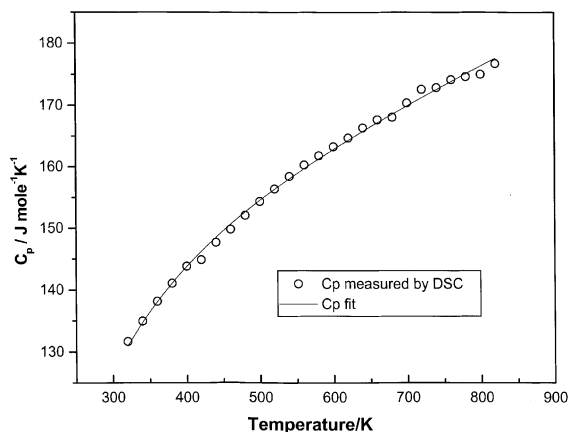| Temperature (K)	C_p (J K^{-1} mol^{-1})		$(H_T^0 - H_{298}^0)$ (J mol^{-1})	S_T^0 (J K^{-1} mol^{-1})	$-(G_T^0 - H_{298}^0)/T$ (J K^{-1} mol^{-1})
	Measured	Fit			
298.15	–	126.3	0	295	295
300	–	126.7	253	296	295
400	143.8	143.8	13861	335	300
500	154.3	154.5	28808	368	311
600	163.2	162.8	44687	397	323
700	170.3	179.8	61325	423	335
800	174.9	176.3	78636	446	348

Fig. 2. Heat capacity data of BaThO$_3$.

the literature for BaThO$_3$ and hence the present work provides the first data for the heat capacity. From Eq. (2) shown above for heat capacity, the enthalpy increments, entropies and Gibbs energy functions were computed. Since no data are available in the literature for the S_{298}^0 value of BaThO$_3$, which was required for the computation of entropies, it was estimated as described below. The $C_{p,298}$ value of BaThO$_3$ determined from our fit is 16.3% higher than the value estimated by invoking Neuman–Kopp's law and using the corresponding values from the literature for ThO$_2$ (61.76 J K^{-1} mol^{-1}) [6]

and BaO (46.77 J K^{-1} mol^{-1}) [7]. Hence it was assumed that the S_{298}^0 value of BaThO$_3$ will also be 16.3% higher than the value computed using Neumann–Kopp's law. The S_{298}^0 values of BaO and ThO$_2$ from the literature used for the estimation are 72.07 [7] and 65.23 [6] J K^{-1} mol^{-1}, respectively. The S_{298}^0 value of BaThO$_3$ thus estimated is 159.7 J K^{-1} mol^{-1}.

The heat capacity data of BaCeO$_3$ measured by DSC and shown in Table 3 are the mean of five or six measurements. The relative standard deviations are in the range 1–2%. The heat flow signal from DSC measurements showed a gradual increase starting from 550 K. This indicates the presence of a second order transition. DTA run on BaCeO$_3$ did not show any signal corresponding to the transition indicating that the heat of the transition is low. The heat capacity values shown in Fig. 3 as a function of temperature also indicate the presence of the transition whose onset temperature is about 500 K. From the area of the peak shown in Fig. 3, the heat of the transition has been computed to be 0.13 kJ mol^{-1}. The measured heat capacity values of BaCeO$_3$ from 320 to 500 K (below the transition) were fitted to the following expression by using the least-squares method

$$C_p \text{ (J K}^{-1} \text{ mol}^{-1})$$
$$= 122.4077 + 1.64 \times 10^{-2} \cdot T - 1.610221 \times 10^6 \cdot T^{-2}$$
$$(320–500 \text{ K}). \tag{3}$$

Table 3
Thermodynamic functions of BaCeO$_3$

Temperature (K)	C_p (J K^{-1} mol^{-1})		$(H_T^0 - H_{298}^0)$ (J mol^{-1})	S_T^0 (J K^{-1} mol^{-1})	$-(G_T^0 - H_{298}^0)/T$ (J K^{-1} mol^{-1})
	Measured	Fit			
298.15	–	109.2	0	134	134
300	–	109.4	219	135	134
400	118.8	118.9	11692	168	139
500	124.3	124.2	23865	195	147
600	126.4				
700	126.3				
800	128.6	133.0[a]			

[a] Computed from Eq. (3).
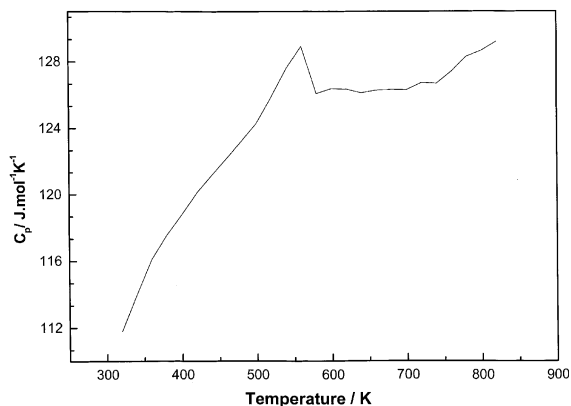
Fig. 3. Measured heat capacity data of BaCeO$_3$ showing the transition.

$BaCeO_3$, the $C_{p,298}$ computed from our fit is in agreement with the value computed from the $C_{p,298}$ values of BaO (46.77 J K^{-1} mol^{-1}) [7] and CeO$_2$ (61.52 J K^{-1} mol^{-1}) [7] from the literature by invoking Neumann–Kopp's rule and hence the S_{298}^0 value of BaCeO$_3$ was also estimated from those of BaO (72.07 J K^{-1}mol^{-1}) [7] and CeO$_2$ (62.3 J K^{-1} mol^{-1}) [7] from the literature by assuming Neumann–Kopp's rule to be valid. The S_{298}^0 value of BaCeO$_3$ thus estimated was 134.37 J K^{-1} mol^{-1}. The heat capacity data at temperatures above 700 K shown in Table 3 were computed from Eq. (3). Though this equation is valid only below the transition, the values extrapolated for temperatures above the transition are only 4% higher than the measured values, as seen in the table.

4. Conclusions

Heat capacity measurements were carried out on BaThO$_3$ and BaCeO$_3$ using DSC in the temperature range 320–820 K. The present data are the first ones for the heat capacity of BaThO$_3$. For BaCeO$_3$, the present data are the first heat capacity data for the temperature range 320–820 K. The present study shows the presence of a second order transition in BaCeO$_3$ whose onset temperature is around 500 K.

Fig. 4. Heat capacity data of BaCeO$_3$.

The standard error of the fit is 0.15. The heat capacity values computed from Eq. (3) are shown in Fig. 4 along with the measured heat capacity data and the extrapolated values of Saha et al. [4]. As seen in the figure, the present data are in agreement with those of Saha et al. [4] within 1–2%. From Eq. (3) shown above for the heat capacity, enthalpy increments, entropies and Gibbs energy functions for the temperature range 320–500 K were computed which are also given in Table 3. For

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