PHYSICAL METHODS OF INVESTIGATION

Thermodynamic Functions of Terbium Hafnate

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Abstract—The molar heat capacity of terbium hafnate with a pyrochlore structure was measured by relaxation and adiabatic calorimetry. The smoothed values of the molar heat capacity were used to calculate the thermodynamic functions in the temperature range 6–330 K. The general form of the Schottky anomaly was determined.

Keywords: terbium hafnate, thermodynamic functions, Schottky anomaly

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INTRODUCTION

Terbium hafnate belongs to the class of high-temperature binary oxides $\text{Ln}_2\text{Hf}_2\text{O}_7$ ($\text{Ln} = \text{La}–\text{Tb}$) with a pyrochlore structure ($Fd3m$). Terbium hafnate crystallizes in the region of continuous series of solid solutions $(1-x)\text{TbO}_{1.5}\cdot x\text{HfO}_2$ ($x \approx 0.45–1.0$) with a disordered fluorite structure ($Fm3m$) based on cubic hafnium dioxide. $\text{Tb}_2\text{Hf}_2\text{O}_7$ undergoes no structural transformations until a temperature of ~ 2500 K, at which it transforms to a disordered fluorite structure [1–3]. As other pyrochlore-structure binary oxides of lanthanides and group 4b metals, terbium hafnate shows great promise as ionic conductors, semiconductors, scintillators, nuclear industry materials, and also substances for design thermal barrier coatings (TBCs) and environmental barrier coatings (EBCs) [4, 5]. Shlyakhtina et al. studied the structural and electrical properties of terbium hafnate [6]. Aung et al. synthesized highly transparent optical ceramics [7], and Yasuhara and Ikesue investigated their magneto-optical properties [8]. Special attention has been given to the formation of nanocrystalline terbium hafnate and its conversion to normal-size crystalline ceramics of the pyrochlore structural type [5, 9–11]. The most interesting study of the set of the physical properties of $\text{Tb}_2\text{Hf}_2\text{O}_7$ pyrochlore in the range 1.8–300 K was made by Anand et al. [12], who explored the magnetic properties, measured the molar heat capacity, and analyzed the increment in the molar heat capacity due to the interaction of the crystal field and 4f electrons of terbium hafnate (Schottky anomaly). Unfortunately, the temperature dependence of the molar heat capacity and the Schottky anomaly were presented in that work [12] only in graphical form and cannot be used for calculations, whereas the molar heat capacity and the thermodynamic functions calculated from it are

highly important characteristics of a substance. The purpose of this work was to measure the molar heat capacity in the temperature range to 330 K and calculate the thermodynamic functions: entropy, enthalpy, and reduced Gibbs energy.

EXPERIMENTAL

Terbium hafnate was synthesized by reverse precipitation. The initial substances were terbium sesquioxide (99.99 wt %, LLC Lankhit), hafnium dioxide (99.99 wt %, LLC Lankhit), hydrochloric acid (35–38 wt %, special-purity grade 20-4, LLC Khimmed), and ammonia solution (25–28 wt % NH_4OH , special-purity grade, LLC Khimmed). The methods of synthesis, measurement of thermal expansion and heat capacity, and processing of results were described in detail previously [13, 14]. The final annealing at 1550 K for 4 h gave $\text{Tb}_{1.994}\text{Hf}_{2.006}\text{O}_{7.003}$. Such a deviation from stoichiometry cannot introduce a significant error to the molar heat capacity [15]. X-ray powder diffraction studies showed that the obtained single-phase sample has a cubic structure of the pyrochlore type with the unit cell parameter $a = 10.455(4)$ Å (Fig. 1), which agrees satisfactorily with the literature data [12, 16]. Scanning electron microscopy demonstrated (Fig. 2) that the sample is not nanosized; therefore, there is no need in making corrections for the size factor. The molecular weight was calculated from the atomic weights [17] and was 786.8265 g/mol. The molar heat capacity was measured by relaxation calorimetry with a Quantum Design PPMS-9 automated physical property measurement system and by adiabatic calorimetry with a BKT-3 automatic low-temperature calorimeter (LLC Termis).

Fig. 1. X-ray powder diffraction pattern of $\text{Tb}_2\text{Hf}_2\text{O}_7$ of the $Fd3m$ (pyrochlore) structural type with $a = 10.455(4) \text{ \AA}$.

Fig. 2. Morphology of the surface of a sample of terbium hafnate (pyrochlore).

RESULTS AND DISCUSSION

The molar heat capacity of terbium hafnate with a pyrochlore structure was measured by relaxation (5.8–43.9 K) and adiabatic (6.0–327.1 K) calorimetry in 38 and 120 temperature points, respectively (Table 1).

The experimental values of the molar heat capacity were smoothed using the following equations [18]:

$$C_p = \sum a_i \ln(T/400)^i \quad (6-15 \text{ K}), \quad (1)$$

$$C_p = 3R \sum a_i \left((\theta_i/T)^2 \right) e^{\theta_i/T} / (e^{\theta_i/T} - 1)^2 \quad (15-330 \text{ K}) \quad (2)$$

Table 2 presents the coefficients of Eqs. (1) and (2).

The dependence of the molar heat capacity in the range 6–330 K is smooth and contains no structural

anomalies. The most interesting region is the low-temperature range (6–25 K, Fig. 3). Here, as in Anand et al. [12], the curve of the molar heat capacity has a minimum ($\sim 2 \text{ J mol}^{-1} \text{ K}^{-1}$) at $\sim 8 \text{ K}$. A further decrease in temperature leads to an increase in the molar heat capacity due to the increasing branch of a magnetic transformation, which occurs at a temperature $< 2 \text{ K}$. This phenomenon is particularly noticeable in comparison with the molar heat capacity of lanthanum hafnate (Fig. 3, curve 4) [19], which has the same structure $Fd3m$. The magnetic transformation in the range 0–2 K is characteristic of all the compounds of lanthanides, except lanthanum and lutetium [20]. At temperatures of 0–6 K, the molar heat capacity is mainly determined by the magnetic component

Table 1. Experimental dependence of the molar heat capacity of terbium hafnate (pyrochlore) on temperature at $p = 101.3$ kPa

T , K	C_p , J mol ⁻¹ K ⁻¹	T , K	C_p , J mol ⁻¹ K ⁻¹	T , K	C_p , J mol ⁻¹ K ⁻¹
Relaxation calorimetry					
5.753	2.368	11.66	3.336	23.89	12.54
6.072	2.320	12.37	3.578	25.19	14.05
6.413	2.290	13.02	3.875	26.61	15.70
6.758	2.265	13.76	4.259	28.19	17.45
7.133	2.268	14.53	4.714	29.76	19.47
7.523	2.273	15.35	5.239	31.45	21.50
7.950	2.318	16.21	5.803	33.23	23.76
8.397	2.361	17.14	6.475	35.12	26.16
8.868	2.438	18.11	7.230	37.12	28.81
9.368	2.547	19.17	8.113	39.22	31.76
9.894	2.690	20.17	9.013	41.47	34.81
10.44	2.854	21.36	10.12	43.86	37.91
11.04	3.060	22.59	11.38		
Adiabatic calorimetry					
6.04	5.44	67.31	70.57	155.49	157.3
6.84	2.83	69.09	72.80	158.98	160.1
7.12	3.43	70.86	74.98	162.48	162.8
7.46	2.95	72.83	77.36	170.24	168.6
7.95	2.85	75.09	80.03	174.24	171.5
8.33	2.58	77.31	82.60	177.77	174.0
8.76	3.21	79.38	84.11	181.31	176.5
9.68	2.86	79.52	85.12	184.83	178.8
10.66	3.24	81.74	87.60	188.36	181.2
11.98	3.44	81.88	88.10	191.90	183.4
13.04	4.22	83.98	90.06	195.53	185.7
14.25	4.65	84.21	88.89	199.11	187.9
15.43	5.42	86.25	92.53	203.09	190.2
16.73	5.82	86.41	92.40	207.48	192.8
18.01	6.45	88.61	94.78	211.96	195.3
19.29	8.04	88.64	95.07	216.39	197.7
20.75	9.60	90.82	97.95	220.76	199.9
23.52	11.52	93.05	99.68	225.14	201.9
25.69	14.00	94.91	101.6	229.51	204.0
27.81	16.58	95.36	102.4	234.05	206.1
29.79	19.10	97.60	105.1	238.47	208.2
31.75	21.67	97.65	104.4	242.89	210.2
33.72	24.37	99.86	106.6	247.23	212.2
35.66	26.79	100.06	106.8	251.58	214.0
37.53	29.62	103.06	109.9	255.87	215.7
39.38	32.38	106.69	113.4	260.16	217.4
41.21	35.06	107.19	113.9	264.42	219.0
43.04	37.45	110.29	117.0	268.67	220.5
44.86	39.85	111.18	117.8	272.87	222.0

Table 1. (Contd.)

T, K	$C_p, J mol^{-1} K^{-1}$	T, K	$C_p, J mol^{-1} K^{-1}$	T, K	$C_p, J mol^{-1} K^{-1}$
46.66	42.57	113.90	120.4	277.04	223.4
48.46	45.24	114.71	121.2	281.21	224.7
50.26	47.51	117.50	123.9	285.30	226.0
52.05	50.02	118.19	124.5	289.38	227.3
53.95	52.58	121.68	127.8	293.45	228.5
56.26	55.82	129.22	134.8	297.48	229.7
58.31	58.68	133.23	138.4	301.39	230.8
60.14	61.18	136.77	141.5	305.84	232.0
61.99	63.67	144.50	148.2	312.25	234.4
63.75	65.99	148.51	151.6	319.75	236.4
65.54	68.31	151.99	154.5	327.08	239.1

Table 2. Coefficients of Eqs. (1) and (2) approximating the temperature dependence of the molar heat capacity of terbium hafnate at 6–330 K and $p = 101.3$ kPa

$C_p = \sum a_i \ln(T/400)^i$ (6–15 K)	
i	a_i
0	355.2435
1	261.9488
2	64.91673
3	5.368378
$C_p = 3R \sum a_i ((\theta_i/T)^2) e^{\theta_i/T} / (e^{\theta_i/T} - 1)^2$ (15–330 K)	
a_i	θ_i
0.12153	7.2915
1.4780	103.628
4.0437	246.615
5.7318	671.243

Fig. 3. Experimental dependences of the molar heat capacity of terbium hafnate (pyrochlore) in the range 6–25 K: (1) adiabatic calorimetry data, (2) relaxation calorimetry data, and (3) smoothing curve (Eqs. (1) and (2)), and (4) molar heat capacity of lanthanum hafnate (pyrochlore) [19].

because the lattice heat capacity of terbium hafnate should be close to the lattice heat capacity of lanthanum hafnate since the difference in molar weight between these substances does not exceed ~5%. The contribution of the low-temperature magnetic component of the molar heat capacity to the increment in the enthalpy at 298 K is typically within the measurement error, whereas the entropy can reach $\Delta S = 2R \ln 2 \approx 11.5 J mol^{-1} K^{-1}$ [20, 21]. However, more accurate determination of the entropy of the magnetic transformation requires additional experiments at very low temperatures. Being unable to measure the molar heat capacity below 6 K, we calculated the thermodynamic functions of terbium hafnate from smoothed values of the molar heat capacity in the range 6–330 K without talking into account the contributions of the values of the functions in the range 0–6 K (Table 3).

Along with the magnetic transformations at very low temperatures, the interaction of 4f electrons with the crystal field leads to an increase in the molar heat capacity of compounds of lanthanides (except compounds of La and Lu) [20–23]. The general form of the excess molar heat capacity can be found by subtracting the lattice heat capacity of terbium hafnate, which, as noted above, differs insignificantly from the molar heat capacity of lanthanum hafnate. Anand et al. [12] performed such a calculation, taking into account that the molar weight of terbium hafnate is larger than that of lanthanum hafnate. However, in our opinion, the upward correction of the lattice heat capacity in weight is not fully justified because the molar heat capacity is dominated by the lanthanide contraction, which acts in the opposite direction, i.e., decreases molar heat capacity [22, 23]. Figure 4 presents the difference

$$\begin{aligned} \Delta C_p (J mol^{-1} K^{-1}) \\ = C_p(Tb_2Hf_2O_7) - C_p(La_2Hf_2O_7), \end{aligned} \quad (3)$$

Table 3. Thermodynamic functions of terbium hafnate (pyrochlore) at 6–330 K and $p = 101.3$ kPa

T, K	$C_p^\circ, \text{J mol}^{-1} \text{K}^{-1}$	$S^\circ(T) - S^\circ(6 \text{ K}),$ $\text{J mol}^{-1} \text{K}^{-1}$	$H^\circ(T) - H^\circ(6 \text{ K}),$ J mol^{-1}	$\Phi^\circ(T) - \Phi^\circ(6 \text{ K}),$ $\text{mol}^{-1} \text{K}^{-1}$
6	2.457	0	0	0
7	2.527	0.3853	2.492	0.0847
8	2.573	0.7266	5.043	0.193
9	2.669	1.036	7.663	0.314
10	2.842	1.326	10.42	0.439
11	3.103	1.609	13.39	0.568
12	3.452	1.894	16.67	0.699
13	3.886	2.187	20.34	0.832
14	4.398	2.494	24.48	0.967
15	4.733	2.801	28.93	0.977
20	8.687	4.661	61.73	1.272
25	13.87	7.142	117.8	1.882
30	19.67	10.18	201.4	2.750
35	25.99	13.68	315.4	3.838
40	32.78	17.58	462.1	5.117
45	39.88	21.85	643.6	6.567
50	47.07	26.43	861.0	8.169
60	61.06	36.26	1402	11.77
70	73.92	46.65	2078	15.78
80	85.64	57.30	2877	20.12
90	96.49	68.02	3788	24.67
100	106.8	78.72	4805	29.39
110	116.6	89.36	5922	34.22
120	126.2	99.92	7136	39.13
130	135.4	110.4	8444	44.09
140	144.2	120.7	9843	49.09
150	152.7	131.0	11330	54.11
160	160.7	141.1	12890	59.13
170	168.3	151.1	14540	64.16
180	175.4	160.9	16260	69.18
190	182.1	170.6	18050	74.18
200	188.3	180.1	19900	79.16
210	194.0	189.4	21810	84.11
220	199.4	198.5	23780	89.04
230	204.4	207.5	25800	93.93
240	209.0	216.3	27860	98.78
250	213.3	224.9	29980	103.6
260	217.3	233.4	32130	108.4
270	221.0	241.6	34320	113.1
280	224.4	249.7	36550	117.8
290	227.6	257.7	38810	122.4
298.15	230.0 $\pm$ 1.2	264.0 $\pm$ 3.0	40670 $\pm$ 220	126.1 $\pm$ 1.5
300	230.5	265.4	41100	127.0
310	233.3	273.0	43420	131.5
320	235.8	280.5	45760	136.0
330	238.2	287.8	48134	140.5
340	240.4	294.9	50527	144.9

Fig. 4. Difference of the molar heat capacities of terbium and lanthanum hafnates.

which gives an idea of the general form of the temperature dependence of the Schottky anomaly for $\text{Tb}_2\text{Hf}_2\text{O}_7$ (pyrochlore). The anomaly has a maximum at ~ 55 K and minimum of ~ 125 K, which fully coincides with the experimental and calculated values of the Schottky anomaly presented in graphical form [12].

CONCLUSIONS

In this work, the molar heat capacity of terbium hafnate of the pyrochlore structural type was measured, and the thermodynamic functions were calculated in the temperature range 6–330 K using the smoothed values of the molar heat capacity. The standard thermodynamic parameters at 298.15 K are the following: $C_p^\circ = 230.0 \pm 1.2 \text{ J mol}^{-1} \text{ K}^{-1}$, $S^\circ(T) - S^\circ(6 \text{ K}) = 264.0 \pm 3.0 \text{ J mol}^{-1} \text{ K}^{-1}$, $H^\circ(T) - H^\circ(6 \text{ K}) = 40670 \pm 220 \text{ J mol}^{-1}$, and $\Phi^\circ(T) - \Phi^\circ(6 \text{ K}) = 126.1 \pm 1.5 \text{ J mol}^{-1} \text{ K}^{-1}$. The general form of the Schottky anomaly was determined.

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CONFLICT OF INTEREST

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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