HEAT CAPACITY OF HAFNIUM MONONITRIDE FROM TEMPERATURES OF 5 TO 350 K
An estimation procedure

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Abstract

Measurements of the heat capacity by quasi-adiabatic, intermittent energy increments from 5 to 350 K show small high heat-capacity anomalies near 7 and 10 K which are attributed to superconducting transitions seen by magnetic measurements on the same carefully synthesized and well-characterized sample of $(Hf_{0.934}Zr_{0.057})(N_{0.97})$. Although no previous heat capacity measurements over the cryogenic region are known, the estimated 298.15 K standard entropy values (S/R) vary in the literature from about 200 per cent higher to 5 per cent lower than our measured value of $(5.28\pm0.01)R^{-1}$ when the formula is represented as above. A simple scheme to represent and predict values based on both molar volumes and atomic masses for related materials is presented which seems more reliable on a limited sample than do others despite the intrusion of lanthanide contraction.

Keywords: entropy, heat capacity, HfN, property prediction, thermal properties

Introduction

Group IV transition metal nitrides are known for their high temperature stability, durability, and hardness. For these metals and the alloys thereof, nitrides are undesirable inclusions which require better fundamental understanding. However, the nitrides themselves are useful functional materials; hafnium nitride coatings have been successfully used on carbide cutting tool substrates, and have been studied for use as solar-absorbing materials [1]. As a binary refractory compound, its low temperature thermophysical properties are of inherent interest.

Although several estimated values for S°_{298} for α-HfN are given in the literature, they vary from about twice the value of this work $(5.28\pm0.01)R$ based on integration of our heat capacities to values somewhat smaller. The classical Latimer approach [2] performed on HfN gives 11.51 R; an early estimate given by Kelley and King [3] is 5.49 R, Spencer [4] gives 5.79 R, which value appears in other compendia [5, 6];

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Grimvall [7] derives an estimate of 5.20 R from his own scheme based upon calculation of his entropy Debye temperature.

Finally, we note that measurements of the magnetic susceptibility over the range of 5 to 20 K show two superconducting transitions: a larger one with maximum slope (χ *vs. T*) at 5.9 K and a much smaller one with maximum slope at 8.7 K. These are consistent with the course of the heat capacity we measured in this region; the increments to the integrated thermophysical values at ambient temperatures are negligible.

Experimental

Sample synthesis and characterization

The sample was prepared by nitridation of hafnium foil with high-purity nitrogen gas. The foil (0.9 inch mil=0.023 mm thick) was derived from hafnium crystal bar of 99.9% minimum hafnium+zirconium. The parent crystal bar had the following analysis: O, <65 ppm; C, <30 ppm; N, 10 ppm; Fe, <51 ppm; Zr, 2.93 mass per cent Zr/(Hf+Zr). Cleaned lengths were creased into a pleated pattern, bundled and inserted into a niobium tube of 2.5 cm internal diameter. This loaded niobium boat was inserted into an alumina tube of 4.45 cm internal diameter within an electrical furnace. The tube was equipped with water-cooled end caps. The apparatus was evacuated and back-filled several times with nitrogen gas (Airco Ultra High Purity grade: <1 ppm oxygen, <1 ppm water, <0.5 ppm total hydrocarbons). The furnace temperature was taken to 1773 *K* at a rate of 500 K h^{-1}, held for 5 h, after which it was allowed to cool at the furnace rate.

During the heating, hold, and cooling phases, a small positive flow of nitrogen was maintained through a sulfuric acid bubbler in parallel with the alumina tube. Following a first such run, the recovered product was in the form of thin, brittle, golden flakes about 90 per cent converted to hafnium nitride. The flakes were lightly pestled in a mortar to pass a 60 mesh screen (250 microns). This material was re-inserted into the furnace in the same niobium boat for a second treatment. That product was analyzed for oxygen and carbon by gas analyzers (LECO combustion method) and found to have 750 mass ppm oxygen and 76 mass ppm carbon. Using these results, together with the zirconium content of the crystal bar, 2.93 mass per cent Zr/(Hf+Zr), nitrogen was determined indirectly by combustion of the nitride to $(H+Zr)O_2$. The ratio of ignited mass to starting mass, 1.0976±0.004, determined a molar N/(Hf+Zr) of 0.97±0.01. The measured oxygen level accounts for just under one per cent, i.e., (N+O)/(Hf+Zr)=0.98. Neglecting minor impurities, the sample can be described as $(Hf_{0.943}Zr_{0.057})N_{0.97}O_{0.01}$. Ignition of the parent foil gave ignited mass/starting mass of 1.1849±0.0004 compared to a calculated value of 1.1844.

Analysis of the sample for metallic impurities resulted in (mass ppm): Al, 110; Cr, <20; Cu, <25; Fe, <50; Mo, <10; Nb, <50; Ni, 29; Si, <25; Ti, <25; W, <0.5; U, 3.0. The aluminum content was possibly acquired during the course of pestling in a Diamonite® alumina mortar and pestle.

X-ray diffraction showed the absence of phases other than the cubic HfN, including Hf_2ON_2 (JCPDS card 39-520), which we have found in earlier attempts to appear in samples at levels of as little at 1500 mass ppm oxygen. Diffraction angles were compared to a silicon internal standard. A cubic lattice parameter a_o=4.516±0.001 Å was determined. This compares to 4.518 Å found by Rudy and Benesovsky [8] for samples said to be 49 atomic percent nitrogen. The value of the lattice parameter may be taken as an index of stoichiometry, since it is known to increase for lesser nitrogen contents [9, 10].

Adiabatic calorimetry

The cryogenic calorimetric heat capacity determinations were made in the Mark XIII cryostat described previously [11], modified by the addition of a guard shield around the adiabatic shield using intermittent electrical work on a 'heater' under quasi-adiabatic, equilibrium conditions. The programming, data logging, and calorimetry were computerized as described elsewhere [12]. A gold-plated (over a nickel film) oxygen-free, high-conductivity, copper calorimeter (designated W-20c) was loaded with 53.606 g of HfN. The buoyancy was calculated on the basis of the molar volume in Table 1. Following evacuation, 5.50 kPa of pressure purified He was added to the sample space to enhance thermal equilibration. The calorimeter was then sealed within a vacuum chamber via a screw cap, which pressed an annealed gold gasket against a circular knife edge on the stainless steel sealing neck of the calorimeter. All measurements of mass, resistance, electrical potential, and time were referred to standardizations and calibrations performed at the then U.S. National Bureau of Standards (now designated as the National Institute of Standards and Technology). Temperatures are judged to correspond with IPTS-48 to within 0.03 K.

The heat capacity of the 13.42 g calorimeter, plus heater and thermometer was determined in a separate series of experiments. The per cent of heat capacity of the sample relative to that of the heater/thermometer and calorimeter assembly was about 71 at 10 K, 55 at 30 K, and 53 to 43 at higher temperatures.

It should be noted that evaluation of the anionic mixing entropy by the ideal classical calculation gives an increment in S^o of the same magnitude as does the small deviation from stoichiometry, but that for the presence of Zr in the Hf metal sheets is more substantial.

Results and discussion

Heat capacity determination

The experimental heat capacities for the measurements are listed in chronological order in Table 1 so the approximation size of the temperature increment can usually be inferred from the adjacent mean temperatures.

Twice the standard deviation in the measured heat capacity is about 1 per cent near 10 K and 0.3 per cent at higher temperatures. The integrated, smoothed,

thermophysical properties derived by integration of the smoothed heat capacity at selected temperatures are given in Table 2. The heat capacity *vs*. temperature plot is presented in Fig. 1.

Table 1 Measured heat capacity of $Hf_{0.943}Zr_{0.057}N_{0.97}$ from 5 to 350 K (R=8.3145 J K^{-1} mol^{-1})

T/K	$C_{p,m}^{\circ}/R$	T/K	$C_{p,m}^{\circ}/R$	T/K	$C_{p,m}^{\circ}/R$
Series I					
5.38	0.001	23.7	0.100	147.36	3.076
5.96	0.015	25.01	0.112	152.92	3.184
6.76	0.001	26.77	0.154	158.49	3.298
7.75	0.001	28.32	0.193	164.08	3.366
8.31	0.001	29.69	0.235	172.64	3.507
8.74	0.001	30.97	0.270	181.38	3.638
9.15	0.001	33.18	0.338	187.31	3.710
9.65	0.001	35.26	0.407	193.25	3.777
10.21	0.009	36.67	0.484	199.19	3.858
10.74	0.007	39.52	0.529	205.13	3.924
11.21	0.001	42.5	0.646	211.08	4.006
12.11	0.001	44.7	0.732	217.12	4.094
13.32	0.002	46.94	0.819	223.19	4.170
14.26	0.002	49.38	0.902	229.45	4.234
15.12	0.002	52.01	1.009	235.62	4.304
16.06	0.002	54.68	1.184	245.39	4.408
16.86	0.002	57.57	1.223	258.76	4.538
17.77	0.003	60.69	1.306	268.22	4.608
Series II		63.78	1.223	275.11	4.684
5.60	0.0011	66.74	1.306	282.21	4.737
7.60	0.011	72.23	1.386	289.32	4.777
9.69	0.011	77.69	1.791	296.40	4.848
10.33	0.011	81.38	1.842	303.55	4.921
11.41	0.007	85.16	2.116	310.67	4.961
12.79	0.009	89.99	2.148	317.78	5.000
14.19	0.014	59.58	2.150	328.49	5.071
15.37	0.016	100.88	2.245	339.16	5.096
16.37	0.022	105.86	2.180	346.29	5.125
17.33	0.024	110.95	2.457		
18.23	0.033	115.98	2.494		
19.50	0.037	120.89	2.606		

Table 1 Continued

T/K	$C_{p,m}^{o}$/R	T/K	$C_{p,m}^{o}$/R	T/K	$C_{p,m}^{o}$/R
22.02	0.042	125.89	2.714		
		130.92	2.816		
		136.28	2.819		
		141.79	2.999		

Table 2 Thermodynamic functions of $Hf_{0.943}Zr_{0.057}N_{0.97}O_{0.01}$ (R=8.3145 J K^{-1} mol^{-1})

T/K	$C_{p,m}^{o}$/R	$\Delta_0^T S_m^{o}$/R	$\Delta_0^T H_m^{o}$/RK	Φ°/R
0	0.000	0.000	0.000	0.000
5	0.001	0.000	0.000	0.000
10	0.007	0.003	0.020	0.001
15	0.020	0.008	0.081	0.002
20	0.053	0.017	0.248	0.005
25	0.120	0.035	0.663	0.009
30	0.242	0.067	1.537	0.016
35	0.406	0.116	3.150	0.026
40	0.579	0.182	5.608	0.041
45	0.755	0.260	8.941	0.061
50	0.929	0.348	13.151	0.086
60	1.260	0.548	24.121	0.146
70	1.558	0.765	38.243	0.218
80	1.820	0.990	55.160	0.301
90	2.050	1.218	74.529	0.391
100	2.254	1.445	96.068	0.484
110	2.441	1.668	119.55	0.582
120	2.617	1.888	114.85	0.681
130	2.788	2.104	171.87	0.782
140	2.956	2.318	200.6	0.884
150	3.123	2.527	230.99	0.987
160	3.288	2.734	263.06	1.090
170	3.450	2.938	296.75	1.192
180	3.605	3.140	332.03	1.295
190	3.753	3.339	368.83	1.397
200	3.891	3.534	407.06	1.499
210	4.019	3.728	446.62	1.601
220	4.136	3.917	487.39	1.701

Table 2 Continued

T/K	$C^{\circ}_{p,m}/R$	$\Delta^{T}_{0}S^{\circ}_{m}/R$	$\Delta^{T}_{0}H^{\circ}_{m}/RK$	Φ°/R
230	4.244	4.103	529.32	1.803
240	4.344	4.286	572.22	1.902
250	4.439	4.465	616.20	2.001
260	4.531	4.641	661.04	2.099
270	4.621	4.815	706.77	2.197
280	4.710	4.984	753.46	2.293
290	4.799	5.151	801.04	2.388
298.15	4.868	5.284	840.34	2.466
300	4.883	5.315	849.39	2.484
325	5.055	5.714	973.81	2.717
350	5.157	6.446	1101.4	2.945

A linear regression analysis was made of the function $C_{p,m}/T$ *vs.* T^2 for curve fitted points from 10.21 to 15.37 K (to avoid the superconducting region) from which the coefficients of the terms linear and cubic temperature were found. From this, values of $\gamma_m=1.20\pm0.3\cdot10^{-3}$ J K^{-2} mol^{-1}; and $\theta^{\circ}_D=484\pm30$ K are found. These compare to values estimated by Grimvall [7] of $2\cdot10^{-3}$ and 510 K, respectively. Hulm and Matthias [13] show T_c varying from about 2 to 9 K, depending on stoichiometry.

Literature reports of the superconductivity give T_c values of 6 to 9 K. T_c's evaluated on the present sample by magnetic susceptibility [14] indicate two superconducting transitions, a weak (i.e., corresponding to a small fraction of the sample) one at 8.7 K, and a larger one whose maximum susceptibility is at 5.9 K. These are consistent with the course of the gross heat capacity we measured in this region (Fig. 1). However, the contribution of these superconductivity increments to the integrated
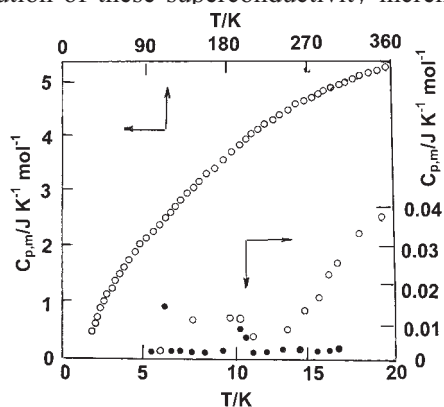
Fig. 1 Heat Capacity of Hf$_{0.943}$Zr$_{0.057}$N$_{0.97}$O$_{0.01}$ Series 1, •; Series 2, o

thermophysical values is negligible by ambient temperatures. The total contribution of the superconductivity ($\Delta_{trs} S_m^o < 0.01R$) represents a contribution to <0.2 per cent of S_m^o (298.15 K).

We choose to characterize our data on the basis of the formula $(Hf_{0.943}Zr_{0.057})(N_{0.98})$ and this compostition with the sum of oxygen and nitrogen represented as $N_{0.98}$ will be used in the definitive tables of thermophysical properties throughout this paper.

The evaluation of the temperature scale and several widely used processes of curve fitting are described in a National Auxiliary Publications Service (NAPS) document No. 07696 [15].

Representation/prediction schemes for heat capacities

The present measurements enhance the discussion of the effect of atomic cation masses entropies on an isostructural and almost an isochoric series. To this end we also consider other interstitial compounds. (Unfortunately, heat capacities of a number of these compounds have been measured only down to near 50 K, and their entropies over the region below had been extrapolated by the original authors from a sum of splines representing Debye and Einstein functions which fit the measured heat capacities above 50 K. We used the Komada Westrum approach [16] using the LEM function to get a more reliable extrapolation.)

The standard entropies of the materials of concern are overwhelmingly dominated by the lattice contribution. The work of Mills [17] recognizes that the entropies of Group IVA nitrides and carbides are close to those of their respective metallic elements, and actually assigns a negative contribution for the interstitial nitrogen and lowering the overestimate of the Latimer method. The scheme of Grimvall [7] employs a single parameter, 'the entropy Debye temperature', θ_s for TiN, estimated from high temperature entropy data by evaluating Debye theta at several temperatures near $T \sim \theta_s$. By adjusting this for the cation mass, he then calculates the value for ZrN as follows:

$$\theta_s(ZrN) = (M_{Zr}/M_{Ti})^{1/4}\theta_s(TiN) \tag{1}$$

A similar equation generates θ_s for HfN; from corresponding data for TiC, values for the carbide series are similarly obtained. S_{298}^o for ZrN is then calculated from tabulated Debye entropy functions whose argument $x = \theta_s(ZrN)/298.15$. Carrying out these calculations for the nitride and carbide series gives entries in the θ_s column and in the right-most column in Table 3 below.

The scheme of the present work seeks to calculate the entropies of each of the series of elements, nitrides and carbides, as adjustments to the Ti member based upon θ_s, molar volume, and cation mass. These parameters are included in Table 3. The elements are an isostructural series (hexagonal, A3) and the nitrides and carbides are all cubic (B1). The standard state entropies, S_m^o are given for series which have substantially reached their equipartition limit, as have the elements, by:

$$S_m^o(\text{Zr or Hf}, 298.15 \text{ K})/R = S^o(\text{Ti}, 298.15 \text{ K})/R + \ln(M_{\text{Zr or Hf}}V_{\text{Zr or Hf}}/M_{Ti}V_{Ti}) \tag{2}$$

For the nitrides and carbides, the heat capacities at 298.15, listed in Table 3 for reference, average only about 75–80% of their equipartition limits. For these, an extra term using the ratio of the θ_ss is added: $\ln(\theta_{TiX}/\theta_{ZrX\text{ or }HfX})$, where X is N or C.

Table 3 summarizes the input data for the above predictive scheme as well as that of Grimvall [7] and lists the experimental values for lattice entropies. The values calculated according to the scheme of this work are seen to be in best accord with the experimental ones.

Table 3 An estimation scheme for prediction of group IVA compounds (R=8.3145 J K^{-1} mol^{-1})

| Substances | Input parameters | | | Measured values | Output (lattice) values | |
	$V_m{}^a/$ cm^3 mol^{-1}	$\theta_s{}^b$	$C_{p,m}$ 298.15 K/ R^c	S_m^o 298.15 K/ R^c lattice	calc. (this research)	calc.^{f} Grimvall [7]
Metals						
Ti	10.634		3.01	3.58	Ref.	
Zr	14.020		3.11	4.57	4.50	
Hf	13.480		3.09	5.15	5.13	
Nitrides						
TiN	11.736	708	4.46	3.56	Ref.	3.65
ZrN	14.441	603	4.87	4.57	4.57	4.35
HfN	13.866	510	4.87	5.15	5.37	5.2
Carbides						
TiC	12.200	808	4.06	2.91	Ref.	2.99
ZrC	15.561	688	4.54^d	3.99	3.96	3.71
HfC	15.017	582	4.51	4.77	4.76	4.53

^{a}Calculated from lattice parameters. Lattice parameters taken from the JCPDS card file [18], except for that of HfN, which was taken from the present work, on grounds of better characterization. (The JCPDS card numbers are: Ti, 5-682; Zr, 5-665; Hf, 38-1478; TiN, 38-1420; ZrN, 35-753; TiC, 32-1383; ZrC, 35-784; HfC, 39-1491)

^{b}Evaluated as in [7]: For the Ti member, entropy data for T>298 K are used to evaluate Grimvall's 'entropy Debye temperatures,' θ_s, which is then mass adjusted using quartic root power dependence on cation mass for the further members

^{c}From [5], except for HfN from this work. Values of C_p^o (298.15 K)/R as an index of the nearness to the equipartition limit of 3nR. (Only values for TiN and TiC are used for Table 3; others are cited for information)

^{d}Pertains to stoichiometry ZrC$_{0.96}$

^{e}For the elements, γ_{el} values from [19] were used to deduct a quantity $S_m^o - S_\gamma^o = S_L^o$; S_T^o=298.15γ from the experimental values to obtain S^o (lattice). For TiN and ZrN these deductions were not made, since the values in the original references were obtained by tabulated Debye and Einstein function extrapolation used to extend trends measured above ~50 K downward. HfN was adjusted using the γ_{el} measured in this work. No adjustments were made to the carbide series

^{f}According to methods of Grimvall [7]

Conclusions

This paper suggests that the empirical scheme proposed (primarily in Table 3) by the present authors provides better agreement of prediction of lattice entropies with measurements of these important quantities than does, for example, the Grimvall [7] approach using his 'entropy Debye temperature method' and provides a scheme to provide reliable estimates of the thermophysical properties of the sub-ambient properties of these useful functional materials.

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