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HIGH-TEMPERATURE HEAT CONTENTS AND ENTROPIES OF SESQUIOXIDES OF LUTETIUM, DYSPROSIUM, AND CERIUM

By L. B. Pankratz and K. K. Kelley

UNITED STATES DEPARTMENT OF THE INTERIOR

BUREAU OF MINES

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HIGH-TEMPERATURE HEAT CONTENTS AND ENTROPIES OF SESQUIOXIDES OF LUTETIUM, DYSPROSIUM, AND CERIUM

by

L. B. Pankratz[1] and K. K. Kelley[2]

ABSTRACT

High-temperature heat-content values of pure lutetium sesquioxide and dysprosium sesquioxide were measured over the temperature range from 298° to 1,800° K. Similar data for cerium sesquioxide were calculated from measurements of a mixture of cerium sesquioxide and dioxide and known values for cerium dioxide.

The results for lutetium sesquioxide are regular. Dysprosium sesquioxide has a minor thermal anomaly near 1,590° K, the extra heat absorption being 220 cal/mole. Hexagonal cerium sesquioxide undergoes a transformation around 1,050° K, which is only slowly reversible; consequently results were obtained for both the low- and high-temperature varieties.

The original heat-content data are reported, and smooth values of heat content and the corresponding entropy increments are tabulated. Equations were derived to represent the heat-content values.

INTRODUCTION

Previous Bureau of Mines papers[3] reported high-temperature heat-content and entropy data for the sesquioxides of erbium, europium, gadolinium,

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[1] Physical chemist, Berkeley Thermodynamics Laboratory, Bureau of Mines, Berkeley, Calif.
[2] Chief, Berkeley Thermodynamics Laboratory, Bureau of Mines, Berkeley, Calif.
[3] King. E. G., W. W. Weller, and L. B. Pankratz. Thermodynamic Data for Lanthanum Sesquioxide. BuMines Rept. of Inv. 5857, 1961, 6 pp.
Pankratz, L. B., E. G. King, and K. K. Kelley. High-Temperature Heat Contents and Entropies of Sesquioxides of Europium, Gadolinium, Neodymium, Samarium, and Yttrium. BuMines Rept. of Inv. 6033, 1962, 18 pp.
Pankratz, L. B., and E. G. King. High-Temperature Heat Contents and Entropies of the Sesquioxides of Erbium, Holmium, Thulium, and Ytterbium. BuMines Rept. of Inv. 6175, 1963, 8 pp.

Work on manuscript completed January 1963.

holmium, neodymium, samarium, thulium, and ytterbium and for the related sesquioxides of lanthanum and yttrium. Data for cerium dioxide also were reported earlier.[4] In continuation of this program, this report contains high-temperature heat content and entropy data for the sesquioxides of lutetium, dysprosium, and cerium, thus completing work on the rare-earth sesquioxides for which adequate samples were available.

Present metallurgical and ceramic interest in the rare-earth elements and compounds makes the continued accumulation of thermodynamic data highly desirable. To our knowledge, no similar previous data exist for the compounds included in this report.

MATERIALS

The lutetium and dysprosium sesquioxides were commercial products having a claimed purity of 99.9 percent. They were used without treatment other than drying in the temperature range from 1,100° to 1,200° C. The X-ray diffraction patterns contained lines of only the cubic varieties of these oxides.

The cerium sesquioxide was prepared at the Reno Metallurgy Research Center of the Bureau of Mines, Reno, Nev., by carbon reduction of 99.9 percent pure cerium dioxide. Carbon content of the product was less than 0.001 percent; the sample also contained 0.02 percent alumina as an impurity. Heat-content measurements were conducted several months after the sample was prepared, and evidently some oxidation occurred during the interim. At the time the measurements were made the sample had the composition $Ce_2O_{3.30}$. This was determined by the increase in mass upon burning to CeO_2 and was confirmed by direct analysis for cerium. The X-ray-diffraction pattern contained the lines of the hexagonal variety of cerium sesquioxide and the principal lines of cerium dioxide.

HIGH-TEMPERATURE HEAT CONTENTS AND ENTROPIES

Heat-content measurements were made with previously described apparatus.[5] The results are expressed in defined calories (1 calorie=4.1840 absolute joules) per mole. Molecular weights accord with the 1961 Table of Atomic Weights.[6]

During the measurements the samples were held in platinum-rhodium capsules, which were sealed gastight by platinum welding. Corrections for the heat contents of the empty capsules were obtained in separate measurements.

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[4]King, E. G., and A. U. Christensen. High-Temperature Heat Contents and Entropies of Cerium Dioxide and Columbium Dioxide. BuMines Rept. of Inv. 5789, 1961, 6 pp.
[5]Kelley, K. K., B. F. Naylor, and C. H. Shomate. The Thermodynamic Properties of Manganese. BuMines Tech. Paper 686, 1946, 34 pp.
[6]Chemical and Engineering News. IUPAC Revises Atomic Weight Values. V. 39, Nov. 20, 1961, pp. 42-43.

Lutetium Sesquioxide

Measured heat-content values for cubic lutetium sesquioxide are listed in table 1 and plotted in figure 1. The results are entirely regular; no evidence of any thermal anomaly was observed.

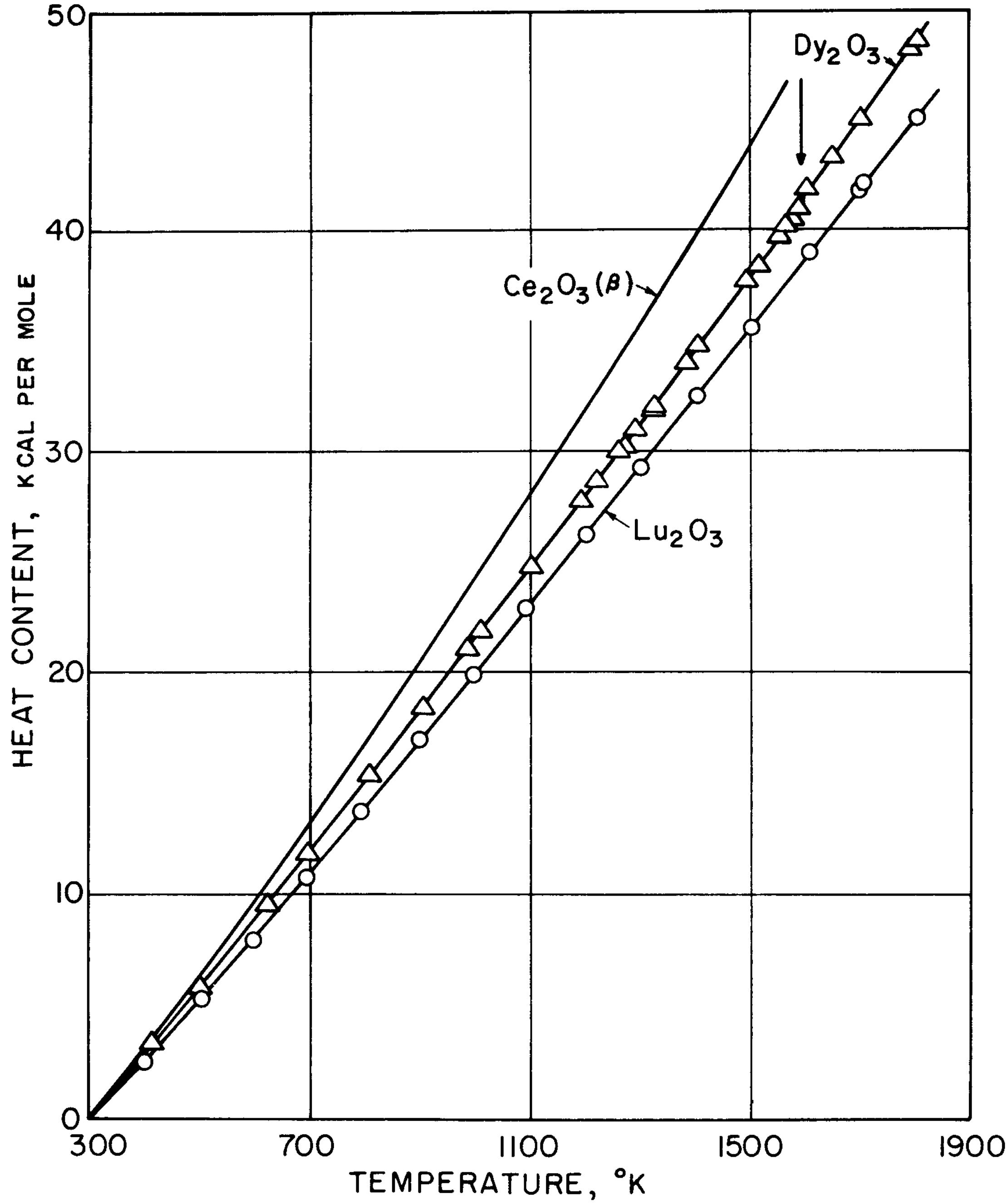

FIGURE 1. - Heat Contents Above 298.15° K.

TABLE 1. - Heat content of cubic Lu_2O_3 (measured values)

T, ° K	$H_T - H_{298.15}$, cal/mole	T, ° K	$H_T - H_{298.15}$, cal/mole	T, ° K	$H_T - H_{298.15}$, cal/mole
400.9....	2,570	994.0....	19,830	1,604.6....	39,050
502.1....	5,320	1,092.1....	22,890	1,695.3....	41,960
596.6....	7,990	1,200.5....	26,210	1,703.1....	42,230
695.6....	10,900	1,301.7....	29,340	1,801.0....	45,170
792.0....	13,750	1,400.6....	32,570	1,801.9....	45,180
897.9....	16,930	1,501.8....	35,720		

Table 2 contains smooth values of the heat content and the corresponding entropy increments. The latter were calculated from the former by the method of Kelley.[7]

TABLE 2. - Smooth heat-content and entropy values for Lu_2O_3 (cubic)

T, ° K	$H_T - H_{298.15}$, cal/mole	$S_T - S_{298.15}$, cal/deg mole	T, ° K	$H_T - H_{298.15}$, cal/mole	$S_T - S_{298.15}$, cal/deg mole
400.....	2,550	7.33	1,300.....	29,340	41.89
500.....	5,260	13.38	1,400.....	32,490	44.23
600.....	8,100	18.55	1,500.....	35,660	46.41
700.....	11,020	23.05	1,600.....	38,840	48.46
800.....	13,990	27.02	1,700.....	42,030	50.40
900.....	17,000	30.56	1,800.....	45,230	52.23
1,000.....	20,040	33.76	1,900.....	48,440	53.97
1,100.....	23,110	36.69	2,000.....	51,660	55.62
1,200.....	26,210	39.39			

The heat content values in table 2 are represented (with an average deviation of 0.1 percent) by the equation

$$H_T - H_{298.15} = 29.38T + 0.88 \times 10^{-3}T^2 + 5.86 \times 10^5T^{-1} - 10,803,$$

which was derived by the method described by Kelley.[8] The corresponding heat-capacity relationship is

$$C_p = 29.38 + 1.76 \times 10^{-3}T - 5.86 \times 10^5T^{-2}.$$

Dysprosium Sesquioxide

Measured heat-content values for cubic dysprosium sesquioxide appear in table 3 and also are shown in figure 1. This substance has a minor thermal anomaly, which first became evident at 1,550° K and was complete at 1,590° K.

[7] Kelley, K. K. Contributions to the Data on Theoretical Metallurgy. XIII. High-Temperature Heat-Content, Heat-Capacity, and Entropy Data for the Elements and Inorganic Compounds. BuMines Bull. 584, 1960, 232 pp.
[8] Work cited in footnote 7.

The extra heat absorption was 220 cal/mole. It is assumed (but not known) that this heat absorption is associated with some intra-atomic phenomenon in the dysprosium ion.

TABLE 3. - Heat content of cubic Dy_2O_3 (measured values)

T, ° K	$H_T - H_{298.15}$, cal/mole	T, ° K	$H_T - H_{298.15}$, cal/mole	T, ° K	$H_T - H_{298.15}$, cal/mole
416.8...	3,430	1,220.1...	28,680	[1]1,560.8...	40,360
500.7...	5,920	1,260.0...	30,070	[1]1,570.1...	40,650
622.4...	9,630	1,269.9...	30,340	[1]1,571.2...	40,690
695.7...	11,930	1,290.0...	31,040	[1]1,585.7...	41,210
805.9...	15,390	1,320.0...	31,950	1,602.0...	41,870
901.3...	18,440	1,323.9...	32,200	1,605.7...	41,970
984.4...	21,080	1,380.1...	34,050	1,650.2...	43,500
1,008.2...	21,870	1,402.5...	34,890	1,697.4...	45,190
1,098.9...	24,800	1,490.5...	37,840	1,791.7...	48,380
1,101.8...	24,880	1,510.6...	38,510	1,801.3...	48,710
1,192.8...	27,800	[1]1,551.0...	39,890		

[1] In transition range.

Smooth values of the heat content and corresponding entropy increments are listed in table 4. In the smoothing process, the data were treated as if there were an isothermal heat absorption at 1,590° K.

TABLE 4. - Smooth heat-content and entropy values for Dy_2O_3 (cubic)

T, ° K	$H_T - H_{298.15}$, cal/mole	$S_T - S_{298.15}$, cal/deg mole	T, ° K	$H_T - H_{298.15}$, cal/mole	$S_T - S_{298.15}$, cal/deg mole
400.....	2,920	8.42	1,400.....	34,720	47.77
500.....	5,900	15.06	1,500.....	38,120	50.11
600.....	8,960	20.64	1,590(α)..	41,220	52.12
700.....	12,070	25.43	1,590(β)..	41,440	52.26
800.....	15,210	29.63	1,600.....	41,780	52.47
900.....	18,380	33.36	1,700.....	45,230	54.57
1,000.....	21,580	36.73	1,800.....	48,680	56.54
1,100.....	24,810	39.81	1,900.....	52,130	58.40
1,200.....	28,070	42.65	2,000.....	55,580	60.17
1,300.....	31,370	45.29			

The heat content values in table 4 for the α-range are represented (with an average deviation of 0.2 percent) by the equation

$$H_T - H_{298.15} = 29.35T + 1.58 \times 10^{-3}T^2 + 2.02 \times 10^5T^{-1} - 9,569.$$

Those for the β-range are represented exactly by the equation

$$H_T - H_{298.15} = 34.50T - 13,420.$$

The corresponding heat-capacity equations are

$$C_p = 29.35 + 3.16 \times 10^{-3}T - 2.02 \times 10^{5}T^{-2}$$

for the α-range, and

$$C_p = 34.50$$

for the β-range.

Cerium Sesquioxide

Measured heat-content values for the cerium sesquioxide-dioxide mixture of composition corresponding to the formula $Ce_2O_{3.30}$ are in table 5. The results are given in calories per formula mass of material (333.04 grams).

TABLE 5. - Heat content of cerium sesquioxide-dioxide mixture ($Ce_2O_{3.30}$) (measured values)

T, ° K	$H_T - H_{298.15}$, cal/mole	T, ° K	$H_T - H_{298.15}$, cal/mole	T, ° K	$H_T - H_{298.15}$, cal/mole
		α-variety			
397.6.....	2,980	698.8....	12,910	899.2....	19,940
399.5.....	3,010	713.4....	13,390	901.6....	20,020
500.2.....	6,240	797.1....	16,300	1,000.5....	23,610
600.8.....	9,580				
		β-variety			
400.3.....	3,190	759.9....	15,440	1,053.0....	26,330
400.4.....	3,160	793.7....	16,700	1,055.6....	26,360
495.6.....	6,290	801.3....	16,980	1,102.7....	28,180
499.9.....	6,450	880.9....	19,910	1,109.7....	28,570
504.5.....	6,580	890.0....	20,200	1,200.8....	31,970
597.8.....	9,790	901.1....	20,620	1,206.7....	32,280
694.7.....	13,120	953.8....	22,590	1,301.8....	36,060
700.9.....	13,350	989.9....	23,920	1,396.3....	39,800
713.3.....	13,760	1,010.1....	24,790	1,501.0....	44,130
745.0.....	14,960	1,030.1....	25,460		

Upon heating this material to 1,050° K, a transformation occurred which was only slowly reversible. The high-temperature variety supercooled upon being dropped into the calorimeter. Consequently, two sets of data were obtained. One set is for the original (low-temperature variety) material and covers the temperature range from 298° to 1,000° K; the other set is for the high-temperature variety and covers the temperature range from 298° to 1,500° K.

As the heat content of cerium dioxide was measured previously[9] and the results showed no anomaly, it was concluded that the transformation was confined to the cerium sesquioxide part of the sample.

In table 5 and in subsequent parts of this report, the letters α and β are used to denote the low and high-temperature varieties.

Heat-content values in table 5 first were smoothed and then corrected for the heat content of the cerium dioxide part by means of the King and Christensen[10] data. The resulting smooth values of the heat content of the two varieties of cerium sesquioxide are in table 6. Figure 1 contains the heat-content curve for the high-temperature variety.

TABLE 6. - Smooth heat-content and entropy values for Ce_2O_3

T, ° K	Ce_2O_3 (α, hexagonal)		Ce_2O_3 (β)	
	$H_T - H_{298.15}$, cal/mole	$S_T - S_{298.15}$, cal/deg mole	$H_T - H_{298.15}$, cal/mole	$S_T - S_{298.15}$, cal/deg mole
400............	3,000	8.63	3,170	9.13
500............	6,150	15.66	6,450	16.44
600............	9,410	21.60	9,840	22.62
700............	12,740	26.73	13,320	27.99
800............	16,140	31.27	16,880	32.74
900............	19,620	35.37	20,520	37.02
1,000............	23,180	39.12	24,250	40.96
1,100............	-	-	28,060	44.59
1,200............	-	-	31,960	47.98
1,300............	-	-	35,940	51.16
1,400............	-	-	40,010	54.18
1,500............	-	-	44,160	57.04

Smooth heat-content values for the α-variety are represented (with an average deviation of 0.3 percent) by the equation

$$H_T - H_{298.15} = 33.26T + 1.34 \times 10^{-3}T^2 + 5.88 \times 10^5T^{-1} - 12,008,$$

which differentiates to give the heat-capacity relationship,

$$C_p = 33.26 + 2.68 \times 10^{-3}T - 5.88 \times 10^5T^{-2}.$$

Heat content values for the β variety are represented (with an average deviation of 0.1 percent) by the equation

$$H_T - H_{298.15} = 30.30T + 3.86 \times 10^{-3}T^2 + 2.22 \times 10^5T^{-1} - 10,122.$$

[9]Work cited in footnote 4.
[10]Work cited in footnote 4.

The corresponding heat-capacity equation is

$$C_p = 30.30 + 7.72 \times 10^{-3}T - 2.22 \times 10^{5}T^{-2}.$$

DISCUSSION

Thermal anomalies, similar to that for dysprosium sesquioxide, were found in previous measurements[11] for the cubic varieties of thulium and ytterbium sesquioxides, for the monoclinic varieties of europium and samarium sesquioxides, and for the hexagonal variety of neodymium sesquioxide. No thermal anomalies were found for the cubic varieties of erbium, europium, gadolinium, holmium, and lutetium sesquioxides, for the monoclinic variety of gadolinium sesquioxide, or for the high-temperature variety of cerium sesquioxide.

Comparing the results in this report with those for the other rare-earth sesquioxides, it is noted that lutetium sesquioxide has about the same average heat capacity as the sesquioxides of erbium, gadolinium, and holmium; dysprosium sesquioxide is similar in average heat capacity to the sesquioxides of thulium and ytterbium; and cerium sesquioxide has the highest average heat capacity of the entire group of compounds.

[11] Work cited in footnote 3.