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High Temperature Heat Contents of Meta- and Orthotitanates of Barium and Strontium

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RECEIVED AUGUST 11, 1952

High temperature heat content measurements of crystalline barium metatitanate, strontium metatitanate, barium orthotitanate and strontium orthotitanate were conducted over the temperature range from 298 to above 1800°K. The results are regular, except those for barium metatitanate, which has a Curie-point near 400°K. involving a small excess heat absorption. Heat content and entropy increment data above 298.16°K. are given in tabular form and heat content equations are derived, for use in the two common methods of making thermodynamic calculations.

Recent papers of Todd and Lorenson[1] presented low temperature heat capacity data and entropies at 298.16°K. for the pure, crystalline meta- and orthotitanates of barium and strontium and for two solid solutions. The present paper reports high temperature heat contents for the same pure titanates from 298.16°K. to temperatures in the range 1820–1832°K.

Materials and Methods

The titanates used in this work were portions of the samples employed by Todd and Lorenson,[1] and the reader is referred to their papers for details of the preparations and analyses.

The heat content measurements were made with apparatus described[2] previously. The substances were enclosed in gas-tight, sealed platinum–rhodium capsules during the measurements. The heat contents of the empty capsules were determined in separate experiments. Frequent calibrations of the furnace thermocouple were made at the melting point of gold, and occasional calibrations at the melting point of palladium.

Results

The measured heat content data are given in Table I, expressed in defined calories (1 cal. = 4.1833 int. joules) per mole. The heat content of barium metatitanate is higher than that of strontium metatitanate by amounts ranging from 3.2 to 6.5%, depending upon the temperature. Likewise, the heat content of barium orthotitanate is higher than that of strontium orthotitanate by 4.7 to 6.0%.

Barium metatitanate has a Curie-point just below 400°K., which has been reported by several previous workers. Blattner and Merz[3] gave 393°K. as the temperature, and 47 cal./mole as the excess heat absorption in the heat capacity "hump." Harwood, Popper and Rushman[4] gave 398°K., and 0.58 cal./deg./mole as the maximum excess heat capacity. Känzig and Meier[5] gave 392°K. and Sawada and Shirane[6] gave 378–388°K. In the region of this Curie-point the structure changes from pseudocubic to cubic, and the dielectric constant and heat capacity pass through maxima.

The heat capacity maximum for barium metatitanate is involved in the present measurements as only a second-order effect, because the excess heat absorption is only a small fraction (*ca.* 2%) of the heat required to warm the substance from 298.16 to 400°K. Examination of the heat content data for this effect necessitates use of some differential method of plotting, such as that in Fig. 1 in which there is plotted

$$\frac{1}{T - 298.16}\left[(H_T - H_{298.16})_{BaTiO_3} - (H_T - H_{298.16})_{SrTiO_3}\right]$$

against T. This function has a cusp-like maximum at about 400°K., which indicates the existence of the Curie-point for barium metatitanate and confirms the magnitude of the heat effect noted by Blattner and Merz. The same figure also shows the analogous function for the barium–strontium orthotitanate combination.

Except for the work cited for barium metatitanate, there are no previously reported high temperature heat content or heat capacity data for these substances. Statton's[7] melting point study of the

TABLE I

HEAT CONTENTS ABOVE 298.16°K. (CAL./MOLE)

T, °K.	$H_T - H_{298.16}$	T, °K.	$H_T - H_{298.16}$	T, °K.	$H_T - H_{298.16}$
$BaTiO_3$ (mol. wt. 233.26)					
355.6	1,450	767.3	13,150	1293.3	29,290
372.4	1,920	869.5	16,180	1364.6	31,520
386.5	2,310	872.5	16,340	1464.3	34,670
408.3	2,920	987.9	19,820	1590.3	38,770
453.7	4,160	1091.0	23,000	1707.5	42,520
557.5	7,070	1198.4	26,360	1831.1	46,560
659.2	10,020	1287.5	29,170		
$SrTiO_3$ (mol. wt. 183.53)					
384.0	2,110	985.5	19,130	1448.7	33,100
463.0	4,170	1089.8	22,310	1538.9	35,850
553.6	6,620	1200.3	25,610	1630.7	38,630
652.8	9,440	1292.6	28,380	1727.9	41,550
762.3	12,550	1342.1	29,920	1831.5	44,790
866.2	15,560				
Ba_2TiO_4 (mol. wt. 386.62)					
397.5	3,670	922.1	26,030	1432.2	48,490
503.1	7,830	1020.4	30,320	1539.4	53,340
594.5	11,620	1120.7	34,720	1631.3	57,420
690.3	15,730	1231.8	39,620	1736.7	62,240
805.3	20,780	1335.3	44,210	1831.3	66,830
807.1	20,830				
Sr_2TiO_4 (mol. wt. 287.16)					
391.8	3,290	938.2	25,110	1432.1	46,330
490.3	7,000	1039.5	29,320	1510.1	49,700
610.7	11,670	1141.9	33,610	1628.2	54,700
719.5	16,120	1265.6	39,030	1726.0	58,930
830.3	20,610	1361.3	43,360	1820.7	63,320

(1) S. S. Todd and R. E. Lorenson, THIS JOURNAL, **74**, 2043, 3764 (1952).

(2) K. K. Kelley, B. F. Naylor and C. H. Shomate, U. S. Bur. Mines Tech. Paper 686 (1946).

(3) H. Blattner and W. Merz, *Helv. Phys. Acta*, **21**, 210 (1948).

(4) M. G. Harwood, P. Popper and D. F. Rushman, *Nature*, **160**, 58 (1947).

(5) W. Känzig and R. Meier, *Helv. Phys. Acta*, **22**, 585 (1949).

(6) S. Sawada and G. Shirane, *J. Phys. Soc. Japan*, **4**, 52 (1949).

(7) W. O. Statton, *J. Chem. Phys.*, **19**, 33 (1951).

TABLE II

HEAT CONTENTS (CAL./MOLE) AND ENTROPIES (CAL./DEG. MOLE) ABOVE 298.16°K.

T, °K.	$BaTiO_3$ $H_T - H_{298.16}$	$BaTiO_3$ $S_T - S_{298.16}$	$SrTiO_3$ $H_T - H_{298.16}$	$SrTiO_3$ $S_T - S_{298.16}$	Ba_2TiO_4 $H_T - H_{298.16}$	Ba_2TiO_4 $S_T - S_{298.16}$	Sr_2TiO_4 $H_T - H_{298.16}$	Sr_2TiO_4 $S_T - S_{298.16}$
400	2,695	7.76	2,530	7.28	3,780	10.88	3,610	10.40
500	5,450	13.90	5,170	13.17	7,730	19.69	7,370	18.78
600	8,290	19.08	7,920	18.18	11,860	27.22	11,270	25.89
700	11,200	23.56	10,750	22.54	16,140	33.81	15,280	32.07
800	14,160	27.51	13,640	26.40	20,520	39.66	19,370	37.53
900	17,170	31.06	16,580	29.86	24,950	44.88	23,520	42.42
1000	20,210	34.26	19,560	33.00	29,380	49.55	27,720	46.84
1100	23,280	37.18	22,560	35.86	33,810	53.77	31,960	50.88
1200	26,380	39.88	25,570	38.48	38,240	57.62	36,230	54.60
1300	29,510	42.39	28,590	40.90	42,670	61.17	40,530	58.04
1400	32,660	44.72	31,620	43.14	47,110	64.46	44,850	61.24
1500	35,840	46.92	34,660	45.24	51,570	67.52	49,180	64.23
1600	39,040	48.98	37,700	47.20	56,060	70.42	53,520	67.03
1700	42,270	50.94	40,750	49.05	60,590	73.17	57,870	69.67
1800	45,540	52.81	43,830	50.81	65,170	75.79	62,230	72.16

$BaO-TiO_2$ system gives 1970 and 1960°K. as the melting points of barium meta- and orthotitanates.

The measured heat content results are represented (to within the average limits of error given in parentheses) by the following equations, which were derived by the method of Shomate[8]:

$BaTiO_3$ (metatitanate):

$$H_T - H_{298.16} = 29.03T + 1.02 \times 10^{-3} T^2 + 4.58 \times 10^5 T^{-1} - 10{,}282 \quad (298\text{–}1800°\text{K.}; 0.3\%)$$

$SrTiO_3$ (metatitanate):

$$H_T - H_{298.16} = 28.23T + 0.88 \times 10^{-3} T^2 + 4.66 \times 10^5 T^{-1} - 10{,}058 \quad (298\text{–}1800°\text{K.}, 0.3\%)$$

Ba_2TiO_4 (orthotitanate):

$$H_T - H_{298.16} = 43.00T + 0.80 \times 10^{-3} T^2 + 6.96 \times 10^5 T^{-1} - 15{,}226 \quad (298\text{–}1800°\text{K.}, 0.6\%)$$

Sr_2TiO_4 (orthotitanate):

$$H_T - H_{298.16} = 38.45T + 1.92 \times 10^{-3} T^2 + 4.67 \times 10^5 T^{-1} - 13{,}201 \quad (298\text{–}1800°\text{K.}, 0.4\%)$$

Table II contains heat content and entropy increments above 298.16°K. at even 100°-values of temperature, for use by those who make thermodynamic calculations in tabular form. The entropy increments were derived, so as to match the heat contents, by the method of Kelley.[9]

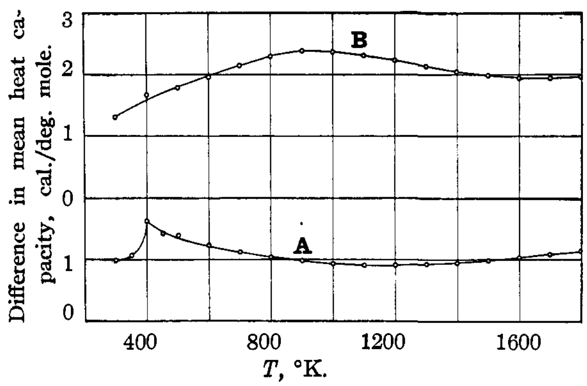

Fig. 1.—Difference in mean heat capacity: curve A, $BaTiO_3$–$SrTiO_3$, curve B, Ba_2TiO_4–Sr_2TiO_4.

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(8) C. H. Shomate, THIS JOURNAL, **66**, 928 (1944).

(9) K. K. Kelley, U. S. Bur. Mines Bull. 476 (1949).