pattern to be obtained. The fact that both $LiO_2H \cdot H_2O$ and Li_2CO_3 are present after treatment of the former with CO_2 tends to make the existence of Li_2CO_4 seem doubtful. It is not surprising that LiO_2H cannot exist at room temperature although Fehler[9] reported that the phase $Li_2O_2 \cdot H_2O_2$ or LiO_2H gave a well-defined Debye pattern.

Dehydration Study of Lithium Hydroxide 1-Hydrate.—The dehydration carried out in a stream of dry helium in the temperature range 125–140° gave anhydrous lithium hydroxide with no intermediate phase as shown by X-ray diffraction patterns and chemical analyses. Dehydration of the hydrate by quickly heating to 445° in the helium stream gave anhydrous lithium hydroxide with no intermediate phase as reported by De Forcrand.[12] On the basis of this work it may be concluded that no intermediate hydrate exists between $LiOH \cdot H_2O$ and LiOH.

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CHINA LAKE, CALIFORNIA

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Heat Capacities at Low Temperatures and Entropies at 298.16°K. of Orthotitanates of Barium and Strontium

BY S. S. TODD AND R. E. LORENSON

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Heat-capacity measurements of crystalline barium and strontium orthotitanates and of their equimolal solid solution were conducted over the temperature range 51 to 309°K. The results are regular, except those for barium orthotitanate in the region above 268°K. where there is evidence of approach to a heat-capacity peak. The entropies at 298.16°K. were obtained as 47.0 ± 0.5, 38.0 ± 0.3 and 45.8 ± 0.4 cal./deg. mole, respectively, for barium orthotitanate, strontium orthotitanate and the equimolal solid solution.

Introduction

In an earlier paper,[1] the authors reported low temperature heat capacities and entropies of crystalline barium and strontium metatitanates and of a solid solution containing 54.3 mole % of the former and 45.7 mole % of the latter. Analogous data for crystalline orthotitanates of barium and strontium and their equimolal solid solution appear in the present paper. No previous, similar data for any of these substances, or for any other orthotitanate, were found in the literature.

Materials.—Barium orthotitanate was prepared from reagent-grade barium hydroxide and titania (99.8% pure, after ignition). Stoichiometric quantities were intimately mixed, pressed into pellets, and heated for prolonged periods at temperatures up to 1350°. As is usual, several grindings, remixings and minor adjustments of composition were made during the preparation process. The final product analyzed 20.80% TiO_2 (as compared with the theoretical 20.67%), 0.34% CaO and 0.02% SiO_2. It is estimated from these results that the purity of this material is 99.2%. The X-ray diffraction pattern gave no evidence of unreacted oxides or of metatitanate. The existence of barium orthotitanate as a compound in the $BaO–TiO_2$ system is shown by the melting-point studies of Statton.[2]

Strontium orthotitanate was prepared in similar fashion from reagent-grade strontium carbonate and titania. Analysis of the final product gave 27.85% TiO_2 (as compared with the theoretical 27.82%), 0.17% CaO and 0.03% SiO_2; and the X-ray diffraction pattern gave no evidence of incomplete reaction. It is estimated that the purity of this material is 99.5%.

The equimolal solid solution was prepared by heating an intimate mixture of the two orthotitanates for prolonged periods at temperatures up to 1400°, with several intervening grindings and remixings. Analysis of the final product gave 23.77% TiO_2, which agrees within the limits of experimental error with the theoretical 23.72% calculated for the equimolal solid solution. The X-ray diffraction pattern was analogous to those for the individual orthotitanates.

Heat Capacities.—The heat capacities were determined with previously described apparatus.[3] The results, expressed in defined calories (1 cal. = 4.1833 int. joules), appear in Table I. Molecular weights accord with the 1949 International Atomic Weights. Sample masses employed in the measurements were 268.45, 217.47 and 250.56 g., respectively, of barium orthotitanate, strontium orthotitanate and the equimolal solid solution.

The heat capacities of strontium orthotitanate and the solid solution follow a regular course throughout the investigated temperature range. Values for barium orthotitanate also are regular between 51 and 268°K. At higher temperatures, the values take on an upward swing, which prevails to 309°K., indicating approach to a heat-capacity maximum. Measurements beyond 309°K. were precluded by temperature limitations of the apparatus. The extra heat absorption up to 298.16°K. is about 10 cal./mole. There is evidence that this upward swing is incompletely reversible. The three consecutive measurements labeled (b), (c) and (d) in Table I were obtained after cooling from 298.7 to 280.0°K. and rewarming to 296.2°K. Measurement (b) falls near normal extension of the results from below the transformation range, whereas (c) and (d) are over 2% higher. The measurement labeled (a) was obtained after heating to 308.9°K., cooling to room temperature, and holding for 4 days. This measurement is similar to (b).

(1) S. S. Todd and R. E. Lorenson, THIS JOURNAL, **74**, 2043 (1952).
(2) W. O. Statton, *J. Chem. Phys.*, **19**, 33 (1951).
(3) K. K. Kelley, B. F. Naylor and C. H. Shomate, U. S. Bur. Mines Tech. Paper 686 (1946).

TABLE I

HEAT CAPACITIES

T, °K.	C_p, cal./deg. mole	T, °K.	C_p, cal./deg. mole	T, °K.	C_p, cal./deg. mole
		Ba_2TiO_4 (mol. wt. 386.62)			
54.00	11.01	136.05	24.99	245.95	33.24
58.42	12.03	146.22	26.06	256.26	33.70
63.14	13.20	156.08	26.99	267.53	34.29
67.85	14.28	166.10	27.88	276.43	34.82
72.35	15.21	176.19	28.73	286.52	35.55
76.82	16.12	185.98	29.51	296.44	35.58 (a)
80.14	16.78	196.00	30.19	296.69	36.37
84.44	17.59	206.36	30.82	298.42	35.66 (b)
94.90	19.38	216.50	31.53	302.62	36.76 (c)
104.75	20.90	226.39	32.11	306.70	37.20 (d)
114.70	22.36	236.14	32.66	298.16	(36.48)
124.79	23.65				
		Sr_2TiO_4 (mol. wt. 287.16)			
53.64	6.634	114.70	18.45	216.73	29.78
58.13	7.589	124.64	19.96	226.24	30.45
62.83	8.649	136.01	21.60	236.33	31.08
67.41	9.666	146.00	22.92	246.02	31.67
71.98	10.61	155.66	24.07	256.22	32.23
76.50	11.53	165.88	25.25	266.67	32.80
80.47	12.35	175.86	26.28	276.38	33.30
85.02	13.24	185.92	27.24	286.49	33.81
94.86	15.07	195.97	28.11	296.66	34.26
104.69	16.76	206.27	28.94	298.16	(34.34)
		0.500 Ba_2TiO_4:0.500 Sr_2TiO_4 (mol. wt. 336.89)			
53.13	8.941	114.75	20.59	216.24	30.62
57.51	9.895	124.63	21.95	226.12	31.29
62.21	11.00	135.95	23.41	236.18	31.87
67.00	12.09	146.05	24.59	245.98	32.47
71.84	13.10	155.74	25.60	256.22	32.96
76.68	14.09	165.93	26.62	266.24	33.47
80.63	14.86	175.93	27.54	276.23	34.00
85.33	15.76	186.03	28.41	286.42	34.50
94.99	17.46	196.03	29.18	296.48	34.82
104.62	19.01	206.41	29.90	298.16	(34.95)

The heat capacity of the equimolal solid solution is virtually identical with the mean of those for the pure orthotitanates between about 200 and 250°K. At lower temperatures, the heat capacity of the solid solution runs higher by about 0.5% at 150°K., 1.2% at 100°K., and 3.8% at 50°K. At higher temperatures, the heat capacity of the solid solution is less than the mean for the pure orthotitanates by about 0.3% at 275°K. and 1.5% at 298°K. The latter deviations are attributable almost entirely to the upward swing of the barium orthotitanate results.

Entropies.—The entropies were calculated in the usual manner. The measured portions, for the range 51 to 298.16°K., were obtained by Simpson-rule integrations of plots of C_p against log T. The extra entropy attributable to the upward swing in the barium orthotitanate heat capacities is less than 0.04 cal./deg. mole at 298.16°K. The entropy increments below 51°K. were obtained by extrapolation, using the empirical Debye and Einstein function sums given below. The function sum for barium orthotitanate fits the measured heat capacity data to within 1.0% at all temperatures below 280°K. Those for strontium orthotitanate and the solid solution fit the measured data over the entire temperature range to within 1.0 and 1.3%, respectively.

Ba_2TiO_4: $D(104/T) + 3E(207/T) + 2E(523/T) + E(858/T)$

Sr_2TiO_4: $D(162/T) + 3E(280/T) + 3E(664/T)$

0.500 Ba_2TiO_4:0.500 Sr_2TiO_4: $D(116/T) + 3E(239/T) + 3E(646/T)$

In the absence of information to the contrary, the equimolal solid solution is assumed to be random and $2R \ln 2 = 2.75$ cal./deg. mole has been added as the entropy of mixing of the barium and strontium ions. The entropy values appear in Table II.

TABLE II

ENTROPIES AT 298.16°K.

Substance	0–51° K., (extrap.)	51–298.16° K., (meas.)	$S_{298.16}$, cal./deg. mole
Ba_2TiO_4	5.94	41.09	47.0 ± 0.5
Sr_2TiO_4	2.81	35.20	38.0 ± 0.3
0.500 Ba_2TiO_4:0.500 Sr_2TiO_4	7.44[a]	38.34	45.8 ± 0.4[a]

[a] Includes entropy of mixing, 2.75 units.

Excluding entropy of mixing, the entropy of the equimolal solid solution deviates by only 0.5 unit from the mean for the pure orthotitanates.

The entropies of formation from the constituent oxides are 1.4 ± 0.8, 0.0 ± 0.5 and 4.0 ± 0.6 cal./deg. mole, respectively, for barium orthotitanate, strontium orthotitanate, and the equimolal solid solution. Values for the oxides from Kelley's[4] compilation were used in computing these results.

BERKELEY 4, CALIFORNIA

(4) K. K. Kelley, U. S. Bur. Mines Bull. 477 (1950).