

Heat Capacity and Thermodynamic Properties of Beryllium Aluminate (Chrysoberyl), $\text{BeO} \cdot \text{Al}_2\text{O}_3$, From 16 to 380 °K*

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The heat capacity of beryllium aluminate (chrysoberyl), $\text{BeO} \cdot \text{Al}_2\text{O}_3$, was determined from 16 to 380 °K and the thermodynamic properties calculated from 0 to 380 °K.

1. Introduction

As a part of the program at the National Bureau of Standards to provide accurate thermodynamic data on the "light-element" compounds, the heat capacities of the compounds of the $\text{BeO}-\text{Al}_2\text{O}_3$ system are being investigated. Thermodynamic data on these compounds should be of interest in high-temperature research and ceramic technology. Although numerous heat-capacity data on BeO and Al_2O_3 have been published [1],¹ no low-temperature heat-capacity data have been found in the literature on any of the mixed-oxide compounds of Be and Al. In this paper, the results of the heat-capacity measurements in the range 16 to 380 °K on beryllium aluminate (chrysoberyl), $\text{BeO} \cdot \text{Al}_2\text{O}_3$, are given. (Henceforth, the name chrysoberyl will be used synonymously with $\text{BeO} \cdot \text{Al}_2\text{O}_3$. Whenever the name beryllium aluminate is used, the chemical formula will be given also for identifying the compound of the $\text{BeO}-\text{Al}_2\text{O}_3$ system to which the reference is made.) Heat-capacity measurements now being made on the compound $\text{BeO} \cdot 3\text{Al}_2\text{O}_3$ will be reported in a future paper.

Beryllium oxide (BeO) and aluminum oxide (Al_2O_3) form two congruently melting mixed-metal oxide compounds, $\text{BeO} \cdot \text{Al}_2\text{O}_3$ and $\text{BeO} \cdot 3\text{Al}_2\text{O}_3$. Lang et al. [2] reported $1870^\circ \pm 10^\circ \text{C}$ and $1910^\circ \pm 10^\circ \text{C}$, respectively, for the melting points of these compounds. Fedoseev [3] reported in addition the compound $3\text{BeO} \cdot \text{Al}_2\text{O}_3$ with an incongruent melting point of 1980 °C. Foster and Royal [4] found $\text{BeO} \cdot \text{Al}_2\text{O}_3$ and $\text{BeO} \cdot 3\text{Al}_2\text{O}_3$ to exhibit very similar optical properties, but distinctive x-ray diffraction patterns. Chrysoberyl occurs in nature in various shades of green, brown, and yellow, or red by trans-

mitted light, with an orthorhombic, dipyramidal crystal structure, space group Pmnb ($a_0=5.47 \text{ \AA}$, $b_0=9.39 \text{ \AA}$, and $c_0=4.42 \text{ \AA}$; all ± 1 percent) [5]. The compounds $\text{BeO} \cdot 3\text{Al}_2\text{O}_3$ and $3\text{BeO} \cdot \text{Al}_2\text{O}_3$ have not been found in nature. The gem variety of chrysoberyl that is red by transmitted light is known as alexandrite and the variety that exhibits chatoyancy, as cat's eye. The color is possibly due to Cr and Fe impurities that have been found. Iron is the usual impurity, substituting for Be and Al in the ferrous and ferric forms, respectively. The ferric form in amounts up to 6 percent by weight Fe_2O_3 has been reported [5]. Titanium has also been reported as an impurity, presumably due to mechanical inclusion of rutile.

2. Sample

The known naturally occurring chrysoberyl samples were considered too impure for the heat-capacity measurements. Semi-Elements, Inc., prepared on request a special sample by arc fusion of a stoichiometric mixture of high-purity BeO and Al_2O_3 powder. The procedure involved the formation of a melted mass within a relatively large charge of the mixture so that the powdered mixture would serve as the "container" for the melted sample to avoid chemical contamination. The fused sample was slowly cooled to room temperature and any material that was not fused adhering to the outer surface was removed mechanically. The fused material was crushed and sieved to collect particles between 10 and 50 mesh sizes (between 0.3 and 2 mm). Microscopic examination showed that these particles were not single crystals.

The material as received contained some particles that appeared gray, presumably from traces of graphite from the electrodes used in the arc fusion process. Qualitative spectrochemical examination

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¹ Figures in brackets indicate literature references at the end of this paper.

of the sample by the Spectrochemical Analysis Section of the National Bureau of Standards showed the limits of percentage impurities given in table 1.

TABLE 1. *Spectrochemical analysis of the beryllium aluminate (chrysoberyl) BeO·Al₂O₃, sample^a*

Element	Percentage limit	Element	Percentage limit
Si	<0.01	Ca	0.001-0.01
Cu	0.01-0.1	V	0.0001-0.001
Ni	0.01-0.1	Sn	<0.001
Fe	0.001-0.01	Pb	<0.001
Mg	0.001-0.01	Ag	<0.0001

^a Analysis by Martha Darr, Spectrochemical Analysis Section of the National Bureau of Standards.

The BeO·Al₂O₃ sample was examined by the petrographic (microscopic) method in the Crystallography Section of the National Bureau of Standards. The size of the crystals was found to be about 200 μ . Since the material was subjected to a grinding process for the microscopic examination, the original BeO·Al₂O₃ crystals in the 10 to 50 mesh polycrystalline particles were, therefore, considered larger than 200 μ . The index of refraction was in agreement with that previously reported for the substance [5]. The crystals were clear but showed some growth defects presumably from rapid crystallization. A small volume of what appeared to be voids was observed. No impurity phases of BeO or Al₂O₃ crystals were found.

The BeO·Al₂O₃ sample was also examined by x-ray diffraction techniques in the Crystal Chemistry Section of the National Bureau of Standards. The diffraction pattern showed several strong lines characteristic of the BeO·Al₂O₃ crystal. No lines characteristic of separate crystalline phases of BeO, Al₂O₃ or BeO·3Al₂O₃ were found. A small amount of impurity phase was observed that could not be identified or its amount estimated from the x-ray results.

Two samples of the material were chemically analyzed for Al and Be by the National Bureau of Standards Analysis and Purification Section. One sample was hand picked to be clear and free from gray coloration; the other was a sample that represented the bulk lot and contained many particles with the gray coloration. The samples were first dissolved in concentrated hydrochloric acid in a sealed ampoule by heating for 24 hr at 250 to 300 °C within a pressurized bomb. A known mixture of BeO and Al₂O₃ was treated in the same manner as a control on the analysis. The aluminum was precipitated as the 8-hydroxyquinolate, Al(C₉H₆ON)₃, after buffering with acetate to the pH of 4.2 to 4.5. The precipitate was ignited to Al₂O₃ and weighed. The beryllium was precipitated as Be(OH)₂ at the pH of 8 to 9 with ammonium hydroxide, ignited to BeO, and weighed. The results of the chemical analyses summarized in table 2 show the sample to be highly pure. The amount of graphite impurity was considered insignificant, and the sample was taken to be 100 percent pure in the processing of the heat-capacity data.

3. Apparatus and Method

The heat-capacity measurements were made in an adiabatic calorimeter similar in principle and design to that described previously [6]. The sample vessel was suspended within the adiabatic shield system by means of a Nylon cord instead of the filling tube shown in the above reference. The adiabatic shields were controlled automatically by means of electronic and electro-mechanical equipment. The details of the calorimeter design and the automatic adiabatic control equipment will be described in a subsequent publication.

TABLE 2. *Chemical analysis of the beryllium aluminate (chrysoberyl), BeO·Al₂O₃, samples^a*

Sample	Percentage by weight		Molar ratio
	Al ₂ O ₃	BeO	Al ₂ O ₃ /BeO
Hand Picked.....	80.25	19.73	0.998
Random.....	80.33	19.72	1.000
Theoretical.....	80.30	19.70	1.000

^a Analysis by Thomas J. Murphy, Analysis and Purification Section of the National Bureau of Standards.

The electrical power input to the calorimeter heater was measured by means of a Wenner potentiometer with reference to saturated standard cells and standard resistors calibrated at the National Bureau of Standards. A volt box was employed for the measurement of the voltage drop across the calorimeter heater. Adjustments were made in the calculation of the power for the current in the volt box and for the resistance of the potential leads from the volt box to the calorimeter heater.

The time interval of heating was determined by means of a precision timer operated on a 60 Hz frequency, furnished at the National Bureau of Standards, that is derived from a 100 kHz quartz oscillator maintained stable within 0.5 ppm. The oscillator frequency is compared and adjusted periodically with the WWV frequency broadcasts.

Temperatures were determined by means of a platinum-resistance thermometer and a high precision Mueller bridge. The thermometer was calibrated by the Temperature Physics Section of the National Bureau of Standards. The calibration above 90 °K was on the 1948 International Practical Temperature Scale [7], and between 10 and 90 °K on the NBS-1955 provisional scale. The provisional scale as it is presently maintained at the National Bureau of Standards, and referred to as degrees K (NBS-1955), is numerically 0.01 deg lower than the NBS-1939 scale [8].

The 1961 atomic weights based on carbon 12 were used to convert the mass of sample investigated to molal basis [9]. Wherever the energy unit calorie is used, the conversion from the cgs unit of energy joule was made using the relation:

$$1 \text{ defined calorie} = 4.1840 \text{ J.}$$

4. Heat-Capacity Measurements and Results

The chrysoberyl sample, being considered quite stable, was poured directly into the calorimeter vessel; that is, the sample was handled exposed to the usual laboratory atmosphere. The vessel with its contents was pumped to a high vacuum and purged with dry helium gas several times and finally sealed with 58 torr pressure of helium gas. The mass of sample investigated was 210.4113 g.

The heat-capacity measurements were made on the calorimeter vessel plus sample from about 16 to 380 °K. This was followed by another series of measurements in the same temperature range on the empty vessel. The analyses and calculations on these measurements were performed on the IBM 7094 computer. Details of the computer codes used will be given in a future publication. Briefly, the analyses and calculations involved the following procedures. From the measurements of initial and final temperatures and the corresponding enthalpy increments, smooth values of heat capacity at regular temperature intervals were obtained for the calorimeter vessel plus sample and for the empty vessel. The heat capacity of the sample was obtained by differencing the smoothed values from the two series of measurements at the corresponding regular temperatures. A correction was made wherever significant for the heat capacity of helium gas. The values of heat capacity of the sample so obtained were smoothed further wherever necessary and finally converted to molal basis. The precision of each series of heat-capacity measurements is shown in figures 1 and 2 in which the deviations of the observed values from the smoothed values are plotted. The relatively large deviation at about 273 °K in both sets of measurements is considered to be due to the melting of a small amount of water sealed unintentionally somewhere in the calorimeter vessel system. Since this anomaly was repeatable in both

sets of measurements, no errors were introduced in the final values of heat capacity of chrysoberyl. Also, the magnitude of the anomaly was less than 0.07 percent of the apparent heat capacity.

Figure 3 shows the plot of the "observed molal heat capacity." Table 3 gives the numerical values. These values were obtained by differencing the heat capacity of the empty vessel and that of the vessel plus sample at the observed temperatures (mid-temperature of the heating interval) of the latter series of measurements. The heat capacity of the empty vessel at the corresponding temperatures was obtained by interpolation in the table of smooth values at regular temperature intervals described earlier. These values were corrected for the heat capacity of the helium gas and for curvature wherever significant and converted to molal basis.

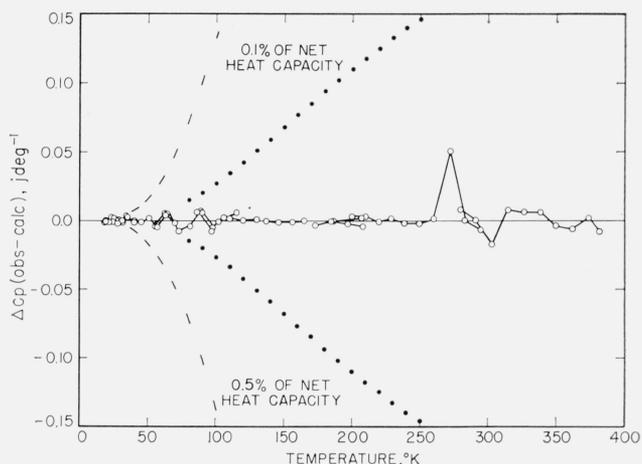


FIGURE 2. Deviations of the heat-capacity measurements on the empty calorimeter vessel used with beryllium aluminate (chrysoberyl), $\text{BeO} \cdot \text{Al}_2\text{O}_3$.

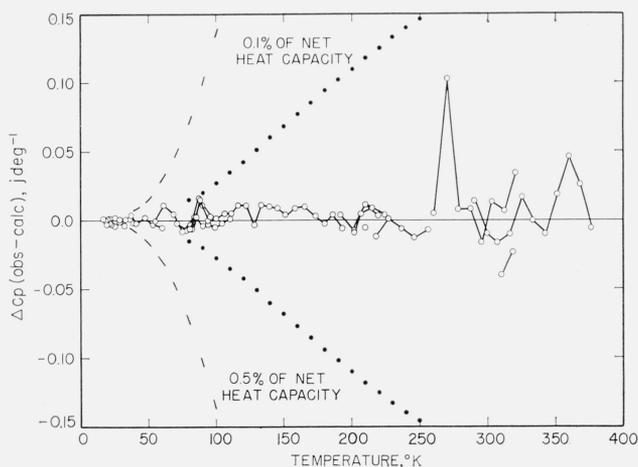


FIGURE 1. Deviations of the heat-capacity measurements on calorimeter vessel plus beryllium aluminate (chrysoberyl), $\text{BeO} \cdot \text{Al}_2\text{O}_3$.

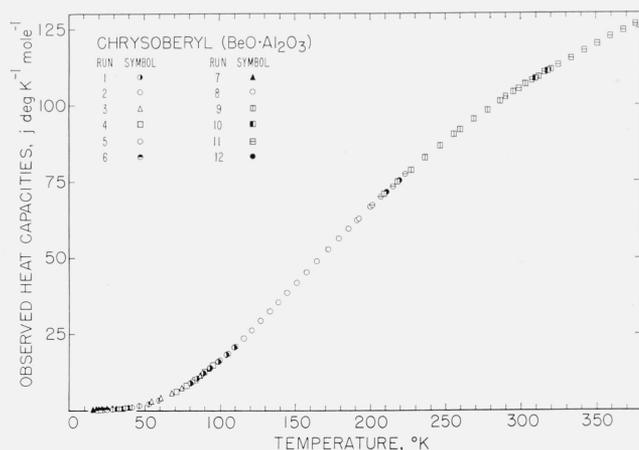


FIGURE 3. Observed values of the molal heat capacity of beryllium aluminate (chrysoberyl), $\text{BeO} \cdot \text{Al}_2\text{O}_3$ as a function of the temperature.

(The numerical values are given in table 3).

TABLE 3. Observed heat capacity of beryllium aluminate (chrysoberyl), $\text{BeO} \cdot \text{Al}_2\text{O}_3$

Gram molecular wt = 126.9728 g, $T \text{ } ^\circ\text{K} = t \text{ } ^\circ\text{C} + 273.15^\circ$

T		C_p		T		C_p		T		C_p	
RUN 1				RUN 5				RUN 9—Con.			
$^\circ\text{K}$	J/deg-mole										
80.5473	9.004	28.7003	0.323	269.0604	95.546	85.1541	10.601	33.3094	.515	277.9055	98.641
89.5817	12.213	37.3141	.742	286.5293	101.591	99.6463	16.223	46.6291	1.550	303.1446	106.945
94.1573	13.972	41.4620	1.043	294.8939	104.322	105.4574	18.746	52.9692	2.382	311.5147	109.488
99.0805	15.979	46.6291	1.550	303.1446	106.945	110.7585	21.160	59.5633	3.521	320.0179	111.988
104.3141	18.235	52.9692	2.382			116.0659	23.675				
109.8372	20.731	59.5633	3.521			121.6485	26.400				
RUN 2				RUN 6				RUN 10			
81.6181	9.368	19.2684	0.092	309.7608	108.934	87.7681	11.557	20.8630	.120	317.7316	111.301
93.6407	13.773	22.8544	.158			99.6463	16.223	25.2148	.216		
105.4574	18.746			RUN 11							
110.7585	21.160	RUN 7				290.0458	102.762				
116.0659	23.675	16.4504	0.045	298.7850	105.567						
121.6485	26.400	18.3613	.079	307.3395	108.215						
127.4847	29.315	20.2893	.112	315.9789	110.797						
133.3266	32.309	22.4282	.152	324.7663	113.340						
139.1501	35.326	25.2495	.213	333.5567	115.764						
145.0459	38.408	28.2888	.306	342.3312	118.096						
151.3929	41.737	31.7145	.438	350.9917	120.335						
158.0993	45.261	35.3961	.626	359.5197	122.458						
165.1286	48.935	39.3311	.877	367.8734	124.451						
172.4762	52.734			376.1640	126.394						
179.4524	56.295	RUN 8				RUN 12					
186.1141	59.649	201.7985	67.283	191.3362	62.230						
193.0372	63.060	207.5974	70.018	201.1287	66.960						
RUN 3				215.3999	73.600	210.4197	71.327				
54.5979	2.637	224.0728	77.459	219.2943	75.347						
61.0699	3.832	RUN 9				RUN 12					
68.1901	5.443	209.6930	70.985								
75.1174	7.308	218.4723	74.970								
81.4060	9.297	227.3537	78.883								
87.3603	11.408	236.6705	82.834								
RUN 4				246.3094	86.771						
70.8972	6.134	255.8343	90.521								
77.5194	8.033	259.9653	92.108								
83.6752	10.081										
89.7941	12.305										
95.9958	14.715										

Considering the precision of the measurements (figs. 1 and 2), the purity of the sample, the accuracy of the various instruments used in the measurements, and the possible systematic errors, the uncertainty in the final values of heat capacity (table 4) was estimated to be ± 0.1 percent between about 80 and 380 $^\circ\text{K}$. Below 80 $^\circ\text{K}$ the uncertainty increased, because of the decrease in the contribution of the sample to the gross heat capacity. At 80 $^\circ\text{K}$, the sample was 40 percent of the total; at 50 $^\circ\text{K}$, 20 percent; at 30 $^\circ\text{K}$, 13 percent; and at 16 $^\circ\text{K}$, the lowest temperature of the measurements, only 6 percent. Below about 40 $^\circ\text{K}$, the decrease in the dR/dT of the platinum resistance thermometer also lowered the accuracy. Considering in addition these factors, the estimated uncertainty is ± 0.3 percent at 50 $^\circ\text{K}$, ± 1 percent at 30 $^\circ\text{K}$, and ± 3 percent at 16 $^\circ\text{K}$.

5. Thermodynamic Functions and Discussion of the Results

The smoothed values of heat capacity at regular temperature intervals were used to derive the various thermodynamic functions. The values of heat capacity below 16 $^\circ\text{K}$, the lower limit of the measurements, were obtained by extrapolation using the equation:

$$C = 1.334 \times 10^{-5} T^3$$

fitted to the observed values at the lower temperatures (below 30 $^\circ\text{K}$). Assuming $C_v = C_p$, the effective Debye characteristic temperature below 30 $^\circ\text{K}$ was calculated to be 1000 $^\circ\text{K}$. The thermodynamic relations involving the heat capacity were evaluated by numerical integration using four-point Lagrangian integration coefficients on the IBM 7094 computer. The thermodynamic functions are given from 0 to 380 $^\circ\text{K}$ in table 4.

Often when the heat-capacity data are not available, an estimate is made by simple addition of the heat capacity of the components that comprise the compound or alloy. A comparison (fig. 4) of the heat

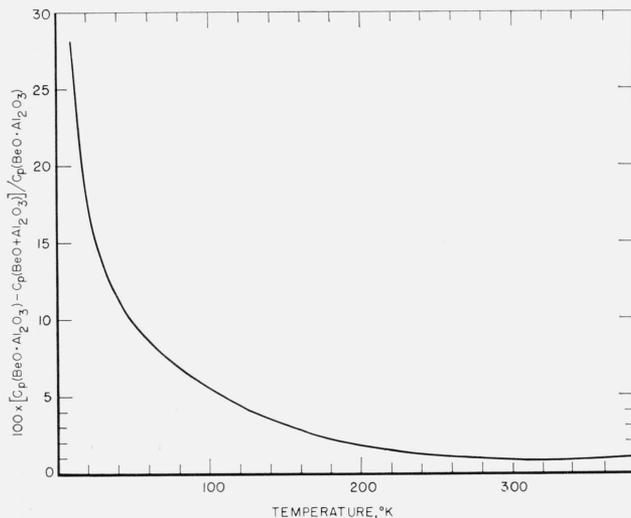


FIGURE 4. Comparison of the heat capacity of beryllium aluminate (chrysoberyl), $\text{BeO} \cdot \text{Al}_2\text{O}_3$, with that of an equimolar mixture of BeO and Al_2O_3 .

capacity of chrysoberyl with that of an equimolar mixture of BeO and Al_2O_3 shows a positive deviation throughout the temperature range (10 to 380 $^\circ\text{K}$). From 200 to 380 $^\circ\text{K}$ the agreement is within about 1 percent. At 100 $^\circ\text{K}$ the deviation is about 5 percent and below this temperature the deviation increases rapidly (28 percent at 10 $^\circ\text{K}$).

This deviation from "additivity" of the heat capacity shown in figure 4 has been found to be typical of most mixed-metal oxides [10]. In the region from about 150 $^\circ\text{K}$ to room temperature and slightly above, the percentage deviation from additivity of most mixed-metal oxides is a few percent

TABLE 4. *Thermodynamic functions for beryllium aluminate (chrysoberyl) (BeO·Al₂O₃) solid phase (at 1-atm pressure)*

Gram molecular wt=126.9728 g, $T^{\circ}\text{K}=t^{\circ}\text{C}+273.15^{\circ}$

T	C_P°	$(H_T^{\circ}-H_0^{\circ})$	$(H_T^{\circ}-H_0^{\circ})/T$	S_T°	$-(G_T^{\circ}-H_0^{\circ})$	$-(G_T^{\circ}-H_0^{\circ})/T$
$^{\circ}\text{K}$	$J/\text{deg-mole}$	$J/\text{deg-mole}$	$J/\text{deg-mole}$	$J/\text{deg-mole}$	$J/\text{deg-mole}$	$J/\text{deg-mole}$
0.00	.000	0.000	0.000	0.000	0.000	0.000
5.00	.002	.002	.001	.001	.001	.000
10.00	.013	.033	.003	.004	.011	.001
15.00	.045	.169	.011	.015	.056	.004
20.00	.107	.534	.027	.036	.178	.009
25.00	.209	1.303	.052	.069	.434	.017
30.00	.367	2.714	.090	.120	.901	.030
35.00	.600	5.099	.146	.194	1.676	.048
40.00	.924	8.865	.222	.294	2.881	.072
45.00	1.366	14.536	.323	.427	4.667	.104
50.00	1.950	22.763	.455	.600	7.215	.144
55.00	2.693	34.301	.624	.819	10.741	.195
60.00	3.599	49.964	.833	1.091	15.492	.258
65.00	4.664	70.555	1.085	1.420	21.745	.335
70.00	5.886	96.865	1.384	1.809	29.793	.426
75.00	7.266	129.68	1.729	2.262	39.944	.533
80.00	8.821	169.82	2.123	2.779	52.518	.656
85.00	10.540	218.17	2.567	3.365	67.850	.798
90.00	12.369	275.40	3.060	4.019	86.281	.959
95.00	14.305	342.03	3.600	4.739	108.15	1.138
100.00	16.365	418.66	4.187	5.524	133.78	1.338
105.00	18.535	505.86	4.818	6.375	163.50	1.557
110.00	20.802	604.17	5.492	7.289	197.63	1.797
115.00	23.152	714.02	6.209	8.265	236.49	2.056
120.00	25.574	835.80	6.965	9.302	280.38	2.337
125.00	28.057	969.86	7.759	10.396	329.60	2.637
130.00	30.589	1116.5	8.588	11.545	384.43	2.957
135.00	33.158	1275.8	9.450	12.748	445.15	3.297
140.00	35.756	1448.1	10.343	14.001	512.00	3.657
145.00	38.372	1633.4	11.265	15.301	585.23	4.036
150.00	40.997	1831.8	12.212	16.646	665.08	4.434
155.00	43.625	2043.4	13.183	18.033	751.76	4.850
160.00	46.247	2268.1	14.175	19.460	845.48	5.284
165.00	48.859	2505.8	15.187	20.923	946.42	5.736
170.00	51.453	2756.6	16.215	22.420	1054.8	6.204
175.00	54.026	3020.3	17.259	23.949	1170.7	6.690
180.00	56.572	3296.8	18.316	25.506	1294.3	7.191
185.00	59.089	3586.0	19.384	27.091	1425.8	7.707
190.00	61.572	3887.7	20.461	28.699	1565.2	8.238
195.00	64.020	4201.7	21.547	30.331	1712.8	8.784
200.00	66.430	4527.8	22.639	31.982	1868.6	9.343
205.00	68.800	4865.9	23.736	33.651	2032.7	9.915

TABLE 4. *Thermodynamic functions for beryllium aluminate (chrysoberyl) (BeO·Al₂O₃) solid phase (at 1-atm pressure)—Con.*

Gram molecular wt=126.9728 g, $T^{\circ}\text{K}=t^{\circ}\text{C}+273.15^{\circ}$

T	C_P°	$(H_T^{\circ}-H_0^{\circ})$	$(H_T^{\circ}-H_0^{\circ})/T$	S_T°	$-(G_T^{\circ}-H_0^{\circ})$	$-(G_T^{\circ}-H_0^{\circ})/T$
$^{\circ}\text{K}$	$J/\text{deg-mole}$	$J/\text{deg-mole}$	$J/\text{deg-mole}$	$J/\text{deg-mole}$	$J/\text{deg-mole}$	$J/\text{deg-mole}$
210.00	71.129	5215.7	24.837	35.337	2205.1	10.501
215.00	73.417	5577.1	25.940	37.038	2386.1	11.098
220.00	75.662	5949.8	27.045	38.752	2575.5	11.707
225.00	77.865	6333.7	28.150	40.477	2773.6	12.327
230.00	80.026	6728.4	29.254	42.212	2980.3	12.958
235.00	82.145	7133.9	30.357	43.956	3195.7	13.599
240.00	84.223	7549.8	31.457	45.707	3419.9	14.249
245.00	86.260	7976.0	32.555	47.465	3652.8	14.909
250.00	88.256	8412.3	33.649	49.227	3894.5	15.578
255.00	90.210	8858.5	34.739	50.994	4145.1	16.255
260.00	92.124	9314.4	35.824	52.765	4404.5	16.940
265.00	93.997	9779.7	36.904	54.537	4672.7	17.633
270.00	95.828	10254.	37.979	56.312	4949.9	18.333
273.15	96.961	10558.	38.652	57.430	5129.0	18.777
275.00	97.618	10738.	39.047	58.086	5235.8	19.039
280.00	99.366	11230.	40.108	59.861	5530.7	19.753
285.00	101.07	11731.	41.163	61.635	5834.5	20.472
290.00	102.74	12241.	42.210	63.407	6147.1	21.197
295.00	104.37	12759.	43.250	65.177	6468.5	21.927
298.15	105.38	13089.	43.901	66.291	6675.6	22.390
300.00	105.96	13285.	44.282	66.945	6798.8	22.663
305.00	107.51	13818.	45.306	68.709	7138.0	23.403
310.00	109.04	14360.	46.322	70.470	7485.9	24.148
315.00	110.52	14909.	47.329	72.226	7842.7	24.897
320.00	111.98	15465.	48.328	73.978	8208.2	25.651
325.00	113.40	16028.	49.318	75.726	8582.4	26.407
330.00	114.79	16599.	50.300	77.468	8965.4	27.168
335.00	116.16	17176.	51.272	79.204	9357.1	27.932
340.00	117.49	17760.	52.237	80.935	9757.5	28.698
345.00	118.79	18351.	53.192	82.660	10166.	29.468
350.00	120.07	18948.	54.138	84.378	10584.	30.240
355.00	121.31	19552.	55.075	86.090	11010.	31.015
360.00	122.54	20161.	56.004	87.795	11445.	31.791
365.00	123.74	20777.	56.924	89.494	11888.	32.570
370.00	124.94	21399.	57.835	91.186	12340.	33.351
373.15	125.68	21794.	58.404	92.248	12629.	33.844
375.00	126.12	22026.	58.737	92.871	12800.	34.133
380.00	127.31	22660.	59.632	94.549	13269.	34.917

H_0° is the enthalpy of the solid at 0°K and 1 atm pressure.

(at most 5 to 10 percent) and fairly constant. Below about 150 or 100 °K, a rapid increase in positive deviation occurs. At 10 °K the deviation is as much as 100 percent. This behavior is interpreted to arise from the contribution to the heat capacity of the additional vibrational degrees of freedom present in the compound becoming predominant at the lower temperatures. Further study on the additivity of the heat capacity is in progress. Below 100 °K, the accuracy of some of the data used in the analysis [10] is somewhat uncertain.

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