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Phase Transformation in Barium Tetraborate

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Orthorhombic BaB_8O_{13} ($a=8.550$, $b=17.352$, $c=13.211$ Å, $D=2.927$ g/cm^3 at 25 °C) transforms reversibly at 700 °C to a high-temperature tetragonal form ($a=8.629$, $c=13.252$ Å, $D=2.906$ g/cm^3) stable from 700 °C to the congruent melting point (889 °C) of the compound. The transition is rapid and probably displacive in character. At the transformation point cell constants change discontinuously, doubling of the b axis is lost and cell contents are reduced from $Z=8$ to $Z=4$. Doubling of the b axis reappears with cooling to the transformation temperature and volume strain is relieved by formation of multiple twins or domains. The latent heat of transformation is 2100 J/mol (0.50 kcal/mol) and $dT/dP=-0.0363$ K/bar.

Key words: BaB_8O_{13}; heat of transformation; orthorhombic form; polymorphism; tetragonal form.

1. Introduction

Barium tetraborate ($BaO.4B_2O_3$) was synthesized by Levin and McMurdie [1][1] in their study of the binary system $BaO-B_2O_3$. The compound was found to melt congruently at 889 °C and was obtained as small crystals, many of which showed multiple twinning. They concluded from optical examination that the material was uniaxial negative, or biaxial negative with small optic axial angle.

Single crystals of BaB_8O_{13} were prepared from the melt by Krogh-Moe [2] and examined by Weissenberg and oscillation x-ray methods. He observed an orthorhombic unit cell with the following lattice constants:

$$a=8.56\text{ Å}$$
$$b=17.38\text{ Å}$$
$$c=13.20\text{ Å}.$$

His calculated density is 2.91 g/cm^3 and there are eight formula units in the cell. The space group was not determined.

Krogh-Moe observed a weak doubling of the b axis which he indicated by writing $b=2\times 8.69$ Å. He reported a pseudo tetragonal symmetry and noted that some of his Weissenberg photographs showed twinning, with the twins having parallel c axes and (010) facing (100). This information suggested to the present authors that BaB_8O_{13} has one or more high-temperature modifications, stable at atmospheric pressure. The objectives of this investigation were: (1) to examine the behavior of the compound when heated from ambient temperatures to the melting point and (2) to characterize any transformations and polymorphs observed.

2. Materials and Methods

Crystalline BaB_8O_{13} was prepared from high purity $BaCO_3$ and H_3BO_3 (purity 99.9%, spectrochemical analysis) by solid state reaction [1]; and by growth from the melt on a high-temperature microscope stage. Seeding of the melt to initiate crystallization was necessary because of supercooling. Small crystals and crystalline powders obtained were studied by differential thermal analysis and by x-ray powder diffractometry from ambient temperatures to 850 °C.

3. Differential Thermal Analysis

Differential thermal analyses were made of crystalline powder samples in milligram quantities. Samples were heated in 1 mil platinum foil dishes (1/4 in diam) in a commercial DTA apparatus. Powdered Al_2O_3 was the reference standard. The heating rate was 10°/min and the sensitivity of the differential temperature scale was 13 μV/in. The alpha to beta inversion of pure quartz at 573.5 °C was used to calibrate the equipment.

An endothermic peak at 700 °C (estimated uncertainty of 5°) was observed for all samples of BaB_8O_{13} when heated from ambient temperatures to the melting point. The effect was rapidly reversible and indicative of the phase transformation; low $BaB_8O_{13}\ \underset{\rightleftarrows}{700\,°C}$ high BaB_8O_{13}. The transformation was confirmed by high-temperature x-ray diffractometry as discussed in section 4.

The heat of transformation was determined by the differential thermal analysis method of Levin and McDaniel [3]. This method is based on the use of weight ratios of sample to a nonreactive internal

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

standard of known heat of transformation. Levin and McDaniel obtained the following relationship for an unknown heat of transformation, ΔH_1:

$$\Delta H_1 = \Delta H_2 \left(\frac{M_1}{M_2}\right) \left(\frac{g_2}{g_1}\right) \left(\frac{A_1}{A_2}\right) \tag{1}$$

where,

ΔH_2 = heat of transformation of the internal standard in kcal/mol

M_1/M_2 = molecular weight ratio of the unknown to the standard

g_2/g_1 = weight ratio of the binary mixture

A_1/A_2 = experimentally determined peak area ratio of the two transformations.

Since this is the equation of a line through the origin with slope $\left(\frac{M_1}{M_2}\right) \times (A_1/A_2)/(g_1/g_2)$, a linear relationship should exist between weight ratios and area ratios over the range that the assumptions in the derivation are valid.

Experimentally determined transformation ratios for binary mixtures of BaB_8O_{13} and quartz (SiO_2) are given in table 1. Figure 1 shows good linearity between transformation area ratios and weight ratios, indicating adherence to theory. The slope of the line (0.250) and its standard deviation (0.0025) were determined by the method of least squares for a line passing through the origin.

Applying equation (1) to $BaB_8O_{13}-SiO_2$ mixtures and using a value of 0.28 kcal/mol (1170 J/mol)[2] for the heat of transformation of alpha to beta quartz:

$$\Delta H_{BaB_8O_{13}} = 0.28 \times \left(\frac{431.82}{60.085}\right) \times 0.250$$
$$= 0.50 \text{ kcal/mol } (2100 \text{J/mol}).$$

TABLE 1. *Ratio of peak areas between low-high transformations in five binary mixtures of* $BaO \cdot 4B_2O_3$ *and quartz as a function of weight ratios*

$BaO \cdot 4B_2O_3 : SiO_2$ (weight ratio)	$A_{BaO \cdot 4B_2O_3} : A_{SiO_2}$ (area ratio)
4 : 1	1.000 0.989 1.018
3 : 1	0.750 .769 .768
3 : 1	0.703 .800 .755
2 : 1	0.473 .451 .469
2 : 1	0.509 .520 .520

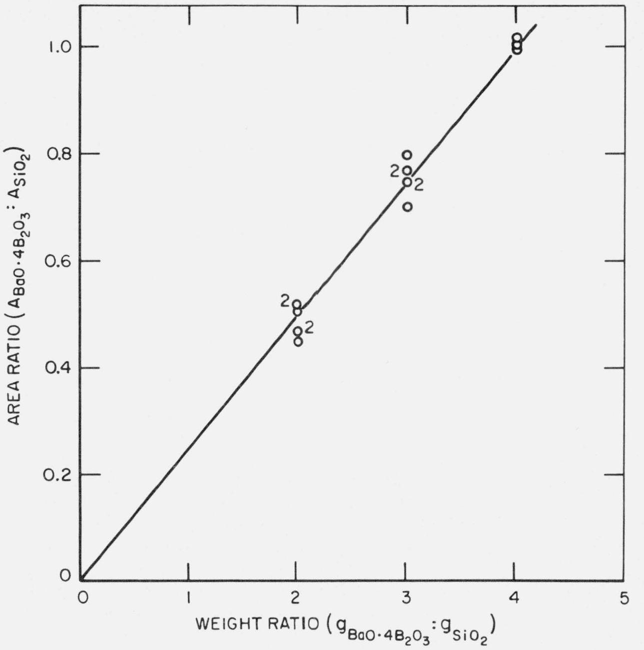

FIGURE 1. *Peak area ratios versus weight ratios for mixtures of* $BaO \cdot 4B_2O_3$ *and* SiO_2 *(quartz). Numbers indicate overlapping data points.*

$y = 0.250x$; $SD_{(slope)} = 0.0025$; $SD_y = 0.028$

4. X-ray Analysis

X-ray powder diffraction patterns were obtained at temperatures from ambient to 850 °C using a modified NBS diffractometer furnace [4] and CuK_{α_1} ($\lambda = 1.54056$Å) radiation. A standard x-ray diffraction pattern of orthorhombic BaB_8O_{13} [5] was used to calibrate the equipment at 25 °C. Unit cell dimensions and their standard errors were refined by a least squares calculation using the program of Evans, Appleman, and Handwerker [6]. Estimated uncertainties in temperature measurements in the x-ray study are of the order of 10 °C on the basis of a transformation temperature of 700 °C determined by differential thermal analysis.

Unit cell dimensions, cell volumes, and densities of four samples of BaB_8O_{13} at selected temperatures are listed in table 2. Least-squares calculations for linear fit of the data were done in three ways, using the OMNITAB programming language [7]: (1) by assigning equal weight to each unit cell dimension; (2) by weighting each determination according to the reciprocal of its standard error, as given in table 2; and (3) by weighting each determination according to the reciprocal of the square of its computed standard error, where the computed standard error is calculated using the linear fit equation for the averaged standard errors at each temperature versus temperature. Differences in results obtained using the three weighting methods were insignificant. A least-squares plot of cell constants as a function of temperature (based on method 3) is shown in figure 2. Dashed

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[2] Private communication, V. B. Parker, Thermochemistry Section, National Bureau of Standards.

lines show the variation in standard error of individual measurements with temperature. Only the standard error of the orthorhombic a axis changes appreciably with temperature (0.006 Å at 25 °C to 0.013 Å at 700 °C). Figure 3 shows a least-squares plot of density as a function of temperature. Equal weights for each determination were used in the calculation. As may be seen in figure 2, the a and c dimensions of orthorhombic BaB_8O_{13} ($a=8.550$, $c=13.211$ Å at 25 °C) increase and b ($b=17.352$ Å, 25 °C) decreases slightly as the temperature of the compound approaches the transformation temperature, 700 °C. At 700 °C, BaB_8O_{13} transforms rapidly and reversibly to a high-temperature tetragonal modification having an a dimension ($a=8.629$ Å) intermediate between a and $b/2$ of the low-temperature orthorhombic form, and with a slightly smaller c axis ($c=13.25$ Å). The doubling of the b axis, reported by Krogh-Moe for the low-temperature form, is lost with change in structure at the transformation and cell contents are reduced from eight to four formula units. X-ray powder diffraction data for the orthorhombic form (at 25 °C) and for the tetragonal form (at 725 °C) are given in table 3. The density increases at the transformation (from 2.891 g/cm³ to 2.906 g/cm³) and then decreases with temperature increase as seen in figure 3. Application of the Clausius-Clapeyron equation, $dT/dP = T\Delta V/\Delta H$ (at one atmosphere), shows an increase in pressure of 1 bar would lower the transition temperature 0.0363 K.

TABLE 2. *Unit cell dimensions and their standard errors, cell volume, and density of* BaB_8O_{13} *at selected temperatures*

Sample	Temp. (°C)	a(Å)	b(Å)	c(Å)	Vol. (Å)³	D(g/cm³)
			Orthorhombic Form			
1	25	8.546 ± 0.003	17.348 ± 0.003	13.234 ± 0.016	1963.5	2.921
2	25	8.550 ± 0.001	17.353 ± 0.003	13.194 ± 0.004	1957.6	2.930
3	25	8.553 ± 0.003	17.350 ± 0.003	13.213 ± 0.005	1960.7	2.925
4	25	8.548 ± 0.003	17.351 ± 0.005	13.214 ± 0.006	1959.8	2.927
1	200	8.551 ± 0.007	17.348 ± 0.008	13.260 ± 0.044	1967.0	2.916
2	200	8.556 ± 0.003	17.356 ± 0.003	13.219 ± 0.006	1962.9	2.922
3	200	8.569 ± 0.003	17.342 ± 0.005	13.304 ± 0.011	1977.1	2.901
1	300	8.567 ± 0.005	17.363 ± 0.005	13.243 ± 0.021	1969.9	2.912
1	400	8.566 ± 0.005	17.339 ± 0.007	13.266 ± 0.023	1978.3	2.911
2	400	8.567 ± 0.007	17.359 ± 0.005	13.267 ± 0.008	1973.8	2.907
3	400	8.572 ± 0.004	17.348 ± 0.005	13.301 ± 0.017	1977.8	2.900
4	500	8.567 ± 0.004	17.360 ± 0.004	13.258 ± 0.020	1970.6	2.911
1	600	8.573 ± 0.003	17.338 ± 0.004	13.292 ± 0.007	1975.8	2.903
2	600	8.601 ± 0.009	17.337 ± 0.005	13.320 ± 0.013	1986.2	2.888
3	600	8.619 ± 0.007	17.325 ± 0.005	13.272 ± 0.009	1981.7	2.894
4	650	8.577 ± 0.008	17.358 ± 0.006	13.294 ± 0.019	1979.2	2.898
2	675	8.601 ± 0.002	17.344 ± 0.004	13.284 ± 0.010	1981.7	2.894
3	675	8.616 ± 0.007	17.326 ± 0.004	13.328 ± 0.006	1989.7	2.884
			Tetragonal Form			
1	725	8.630 ± 0.001	....	13.268 ± 0.004	988.2	2.902
2	725	8.636 ± 0.001	....	13.279 ± 0.005	990.3	2.896
3	725	8.635 ± 0.001	....	13.292 ± 0.007	991.1	2.893
1	750	8.630 ± 0.001	....	13.288 ± 0.006	989.8	2.898
4	750	8.639 ± 0.002	....	13.252 ± 0.008	989.0	2.900
3	775	8.638 ± 0.003	....	13.345 ± 0.015	995.9	2.880
1	800	8.641 ± 0.002	....	13.326 ± 0.006	995.1	2.882
2	800	8.643 ± 0.001	....	13.337 ± 0.006	996.3	2.878
1	850	8.652 ± 0.002	....	13.376 ± 0.005	1001.2	2.865

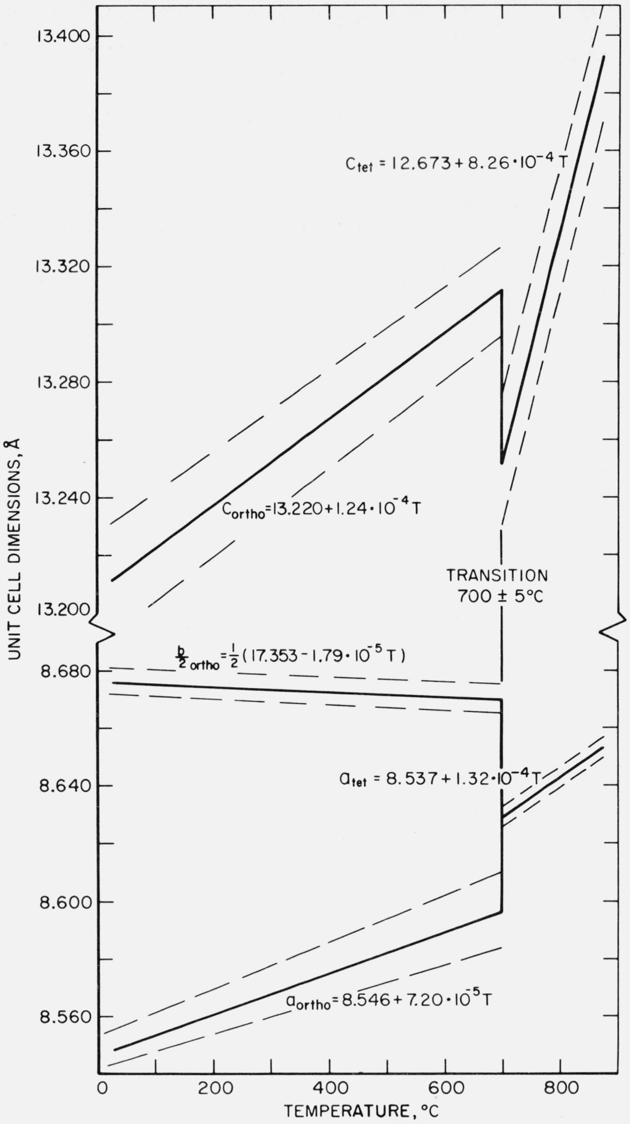

Figure 2. *Unit cell dimensions of* $BaO \cdot 4B_2O_3$ *as a function of temperature.*

Selected standard deviations of single measurements are:

(Orthorhombic form)		(Tetragonal form)	
25 °C	700 °C	700 °C	800 °C
$SD_a = 0.006$ Å	0.013 Å	$SD_a = 0.003$ Å	0.004 Å
$SD_b = 0.010$ Å	0.010 Å	$SD_c = 0.024$ Å	0.023 Å
$SD_c = 0.019$ Å	0.015 Å		

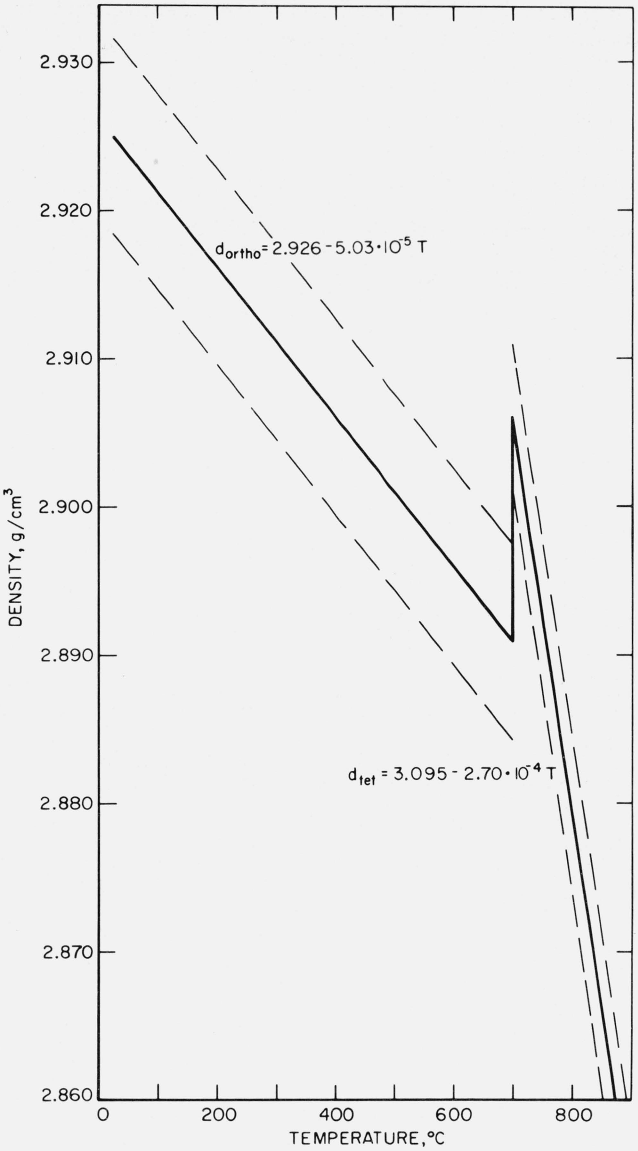

Figure 3. *Density of* $BaO \cdot 4B_2O_3$ *as a function of temperature.*

(Orthorhombic form)	(Tetragonal form)
$SD_d = 0.0066$ g/cm³	$SD_d = 0.0051$ g/cm³

Table 3. *X-ray powder diffraction data for orthorhombic and tetragonal* BaB_8O_{13}

Orthorhombic BaB_8O_{13} (25 °C)[a]				Tetragonal BaB_8O_{13} (725 °C)[b]				
$a = 8.550 \pm 0.001$ Å[c] $b = 17.352 \pm 0.002$ Å $c = 13.211 \pm 0.003$ Å $D_{(calc)} = 2.927$ g/cm³ $Z = 8$				$a = 8.630 \pm 0.001$ Å[c] $c = 13.268 \pm 0.004$ Å $D_{(calc)} = 2.899$[d] g/cm³ $Z = 4$				
d(Å)	I	hkl	2θ(°)	d(Å)	I	hkl	$2\theta(°)_{obs}$	$2\theta(°)_{calc}$
7.25	10	021	12.20					
6.09	55	120	14.54	6.10	55	110	14.50	14.50
5.24	100	102	16.92	5.25	35	102	16.85	16.84
4.35	6	040	20.42	4.32	11	200	20.55	20.56
4.277	5	200	20.75					
4.120	13	041	21.55					
4.068	8	201	21.83	4.107	13	201	21.62	21.64
3.916	6	103	22.69					
3.872	13	140	22.95					
3.836	6	220	23.17	3.859	8	210	23.03	23.03
3.714	13	141	23.94					
3.682	5	221	24.15	3.702	9	211	24.02	23.99
3.625	5	042	24.54					
3.590	7	202	24.78	3.616	8	202	24.60	24.59
3.572	9	123	24.91					
3.515	2	212	25.32					
3.337	95	142	26.69					
3.316	100	222	26.86	3.337	78	212	26.69	26.70
3.124	3	151	28.55					
3.081	14	104	28.96	3.096	5	104	28.81	28.81
3.047	30	240	29.29	3.050	30	220	29.26	29.25
2.965	2	241	30.12					
2.904	80	124	30.77	2.904	29	114	30.63	30.65
2.895		060, 223	30.86					
2.826	4	061	31.64					
2.740	25	160	32.65					
2.709	25	320	33.04	2.730	28	310	32.78	32.79
2.683	11	161	33.37					
2.650	16	321, 062	33.80	2.673	14	311	33.50	33.50
2.617	25	302	34.24	2.640	20	302	33.93	33.94
2.531	5	162	35.43					
2.524	6	105	35.54	2.535	4	105	35.38	35.36
2.510	7	144	35.75					
2.502	9	224	35.86	2.517	7	214	35.64	35.66
2.418	5	063	37.15					
2.393	4	303, 054	37.56					
2.380	3	234, 170, +	37.76					
2.346	3	341, 171	38.34					
2.326	4	163	38.68					
2.306	4	323	39.02					
2.251	30	262	40.02					
2.241	50	342	40.20	2.252	67	322	40.00	40.01
2.238		244	40.27					
2.169	14	080	41.60	2.155	17	400	41.88	41.83
2.138	20	400	42.23					
2.132	25	026, 106	42.35					
2.122	8	410	42.56					
2.111	11	401, 164	42.81					
2.105	17	263, 180, +	42.93					
2.094	19	173, 324, +	43.17	2.107	23	314	42.89	42.88

TABLE 3. *X-ray powder diffraction data for orthorhombic and tetragonal* BaB_8O_{13} (Continued)

Orthorhombic BaB_8O_{13} (25 °C)[a]				Tetragonal BaB_8O_{13} (725 °C)[b]				
d(Å)	I	hkl	$2\theta(°)$	d(Å)	I	hkl	$2\theta(°)_{obs}$	$2\theta(°)_{calc}$
2.076	7	181, 420	43.57	……	……	……	……	……
2.050	6	421	44.13	……	……	……	……	……
2.033	3	402	44.52	……	……	……	……	……
2.003	10	182, 136	45.24	……	……	……	……	……
1.980	12	422	45.79	1.996	23	412	45.40	45.40

[a] Data from NBS standard pattern (CuK_{α_1}, $\lambda = 1.54056$ Å, W standard, $a = 3.16516$ Å). [5]

[b] From sample 1, table 2.

[c] Unit cell constants and their standard errors are based on least-squares refinement of the variance-covariance matrix derived from the unweighted $\Delta\theta$ residuals.

[d] Calculated with equation given in figure 3.

5. Summary and Conclusions

Orthorhombic BaB_8O_{13} transforms reversibly at 700 ± 5 °C (and one atmosphere) to a high-temperature tetragonal modification, stable from 700 °C to the congruent melting point (889 °C) of the compound. The transformation is rapid and probably displacive, with changes in second coordination bonds. If the transformation is displacive, it provides an example of a transformation in which the high-temperature form has a slightly smaller specific volume than the low-temperature form as compared with Buerger's listed criteria for displacive polymorphs [8] in which the reverse is true. At the transformation point all cell constants change discontinuously, the original b axis is halved and the cell contents are reduced from eight to four formula units. The doubling reappears when the high-temperature form is cooled to the transformation temperature, and the resulting volume strain is relieved by formation of multiple twins or domains. The latent heat of transformation is 2100 J/mol (0.50 kcal/mol), as compared with 1170 J/mol (0.28 kcal/mol) for the alpha to beta quartz transformation, and $dT/dP = -0.0363$ K/bar.

6. References

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