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THERMOCHEMICAL STUDIES OF GROUP IIIB BORATES AND MIXED BORATES

M. SWEENEY
University of the West Indies (Trinidad)
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ABSTRACT

The changes in energy, mass and structure of Sc, Y, La and In borate were studied at temperatures up to 1400 °C with and without the solid diluents, alumina and magnesia. These compounds did not decompose, but based on the energetics of solid state transitions, the stability of the crystal lattice was found to be: $ScBO_3 \simeq LaBO_3 \simeq InBO_3 > YBO_3$. YBO_3 was found to be dimorphic. The high temperature form being the pseudohexagonal vaterite structure. $LaBO_3$ formed a solid solution with this structure. The reverse transition took place with considerable hysteresis.

INTRODUCTION

The use of differential thermal analysis (DTA) to study changes in energy, thermogravimetric analysis (TG) to study changes in mass, and X-ray diffraction patterns to study changes in structure can be combined to give a comprehensive picture of chemical reactions in solid and liquid states as the temperature is raised.

The object of this work is to study and compare the changes in energy and mass of these substances as the temperature is raised at a constant rate to 1400 °C. X-ray diffraction has been used to identify the various materials recovered from the reactions. High temperature X-ray diffractions and thermal microscopic analyses (TMA) were used as complementary methods in the study of YBO_3.

There are two main crystalline forms of these compounds which exhibit the calcite or aragonite structures. A third crystalline form known as vaterite has been observed as a high temperature–high pressure structure. In this structure each metal atom is surrounded by four oxygen atoms as compared with six and nine oxygen atoms in calcite and aragonite structures, respectively.

Goldschmidt et al.[1] prepared and investigated the crystal structures of these trivalent metal borates and showed that: YBO_3, $ScBO_3$ and $InBO_3$ were of the calcite type and $LaBO_3$ of the aragonite type at room temperature.

EXPERIMENTAL

Apparatus

The DTA apparatus used was the Model 10Mh of R. Stone and Co.[2]. The TG work was done on a Stanton thermobalance. The X-ray unit was a Norelco watercooled unit, North American Philips. The TMA work was done on a Leitz-Wetzlar Ortholux II polarizing microscope which was fitted with a microfurnace. The temperature of the furnace was regulated with a transformer and observed on a galvanometer. A Leica 35 mm camera was used to photograph the substances under investigation.

A hot-stage was designed and built for the X-ray unit. A heating coil was made from Chromel A wire and was covered with fire-proof cement. The power input was controlled with a regulating transformer. This miniature furnace was calibrated both by a thermocouple–galvanometer system and with an optical pyrometer. Both methods showed that the temperature could be controlled to within ±10°C.

A miniature DTA apparatus was also built. Two quartz tubes were imbedded in some fire-proof cement. A heating coil was placed around this block. This system was then cemented in an alumina crucible. The furnace was insulated with powdered asbestos. A Pt–Pt/10% Rh thermocouple was installed in each of the quartz cells. The thermocouple leads were attached in series to a double-pole–double-throw switch. Connections were made from the DPDT switch to a Leeds and Northrup No. 7551 potentiometer. A standard cell, a galvanometer, a transformer and three $1\frac{1}{2}$ V dry cell batteries, completed the circuit for this apparatus.

An open furnace was used on the DTA apparatus. A "Hevi-Duti" electric furnace was used to preheat some samples of YBO_3 in an attempt to quench its high temperature structure.

In order to ascertain the depability of our DTA results, a sample of YBO_3 was analyzed by a technician in the Chemical Engineering Department, N.S. Technical College on their DTA apparatus. A heating rate of 10°C min^{-1} was also used.

Sample

The samples could not be purchased. They were prepared from boric acid and their respective metal oxide following Goldschmidts[1] procedure. An induction furnace was used to heat these mixtures. X-ray diffraction patterns were made at 8-h intervals until they showed no changes in *d*-spacing of two successive tests. DTA and TG curves were also run on the initial mixtures.

YBO_3 was prepared by mixing equivalent amounts of Y_2O_3 and H_3BO_3 or Y_2O_3 and B_2O_3 and heated to 1000°C as follows:

(i) The mixture was pressed into pellets and heated at 1000°C for several hours in an induction furnace.

(ii) The mixture was heated to above 1000°C in a DTA apparatus.

(iii) The mixture was heated to above 1000°C in a thermal balance.

(iv) The mixture was heated under pressure for several hours.

$YLa(BO_3)_2$ was prepared by mixing 80, 50, and 20 mol % Y_2O_3 with 20, 50, 80 mol % La_2O_3 with equivalent amounts of H_3BO_3. These were titurated, pressed into pellets and heated at 1000°C for several hours. X-ray diffraction patterns were made of the resulting substance, and of the residue after heating three to five times to around 1300–1400 °C in the DTA apparatus.

All materials were ground and sieved to 140–300 mesh size. Runs were carried out under three conditions, viz.: (a) Undiluted samples; (b) samples diluted with calcined alumina; and (c) samples diluted with calcined magnesia.

RESULTS AND DISCUSSION

Some of the data obtained by the DTA and TG studies of the borates are shown. No weight loss was observed for any of the borates, $ScBO_3$, YBO_3, $LaBO_3$ or $InBO_3$.

The thermal stabilities of the borates are very high and no decomposition nor fusion occurred. The DTA curves showed no reaction peaks for any of the borates with the exception of YBO_3 (Fig. 1). They were all found to melt at around 2000 °C.

Investigation of the original mixtures of oxides and boric acid indicated (Table 1 and Figs. 1–4) that on first heating H_3BO_3 melted and H_2O was released at

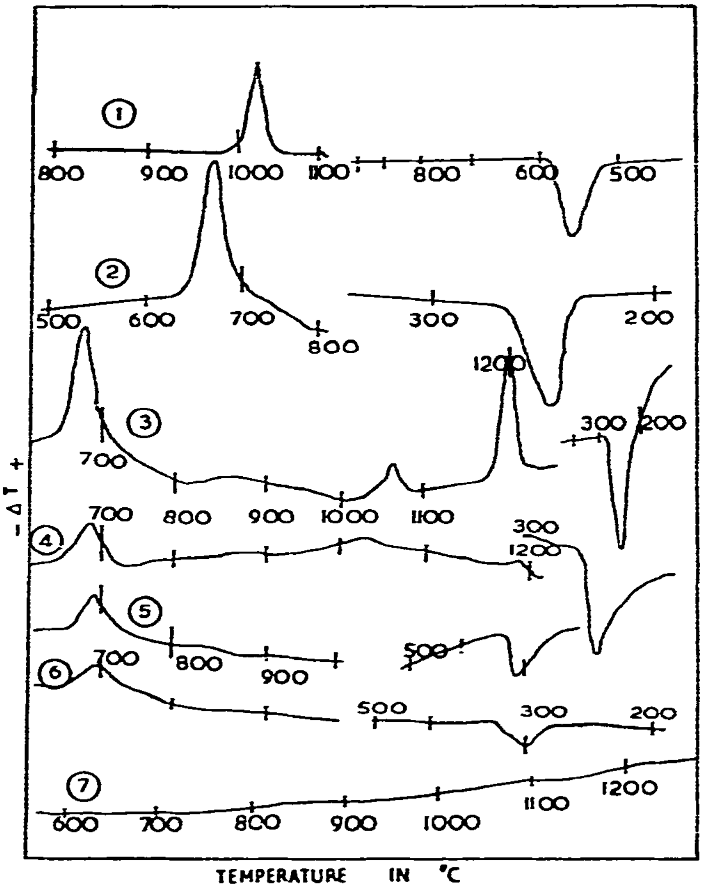

Fig. 1. DTA curves (heating and cooling) for (1) = YBO_3; (2) = 80:20 $YLa(BO_3)_2$; (3) = 50:50 $YLa(BO_3)_2$—1st heating and cooling; (4) = 3rd heating and cooling; (5) = 20:80 $YLa(BO_3)_2$—1st heating and cooling; (6) = 2nd heating and cooling; (7) = $LaBO_3$.

TABLE 1

DTA PEAK TEMPERATURES OBTAINED FOR INITIAL MIXTURES USED IN BORATE FORMATIONS (1) AND RESIDUES RE-ANALYSED (2)

	Sample	*Endotherm*	*Exotherm*
(1)	$Sc_2O_3 + H_3BO_3$	173, 185	736
(2)		—	—
(1)	$Y_2O_3 + H_3BO_3$	173, 185	620
(2)		1021	—
(1)	$La_2O_3 + H_3BO_3$	173, 430	630, 715, 760
(2)		—	—
(1)	$In(OH)_3 + H_3BO_3$	173, 185, 326, 370, 600	
(2)		—	—

175 and 185°C. In the mixture of $In(OH)_3 + H_3BO_3$ there was a double-peaked endotherm between 300 and 400°C resulting from the loss of water from $In(OH)_3$ (Fig. 2). On repeated heatings, only the mixture with yttrium gave a sign of further reaction.

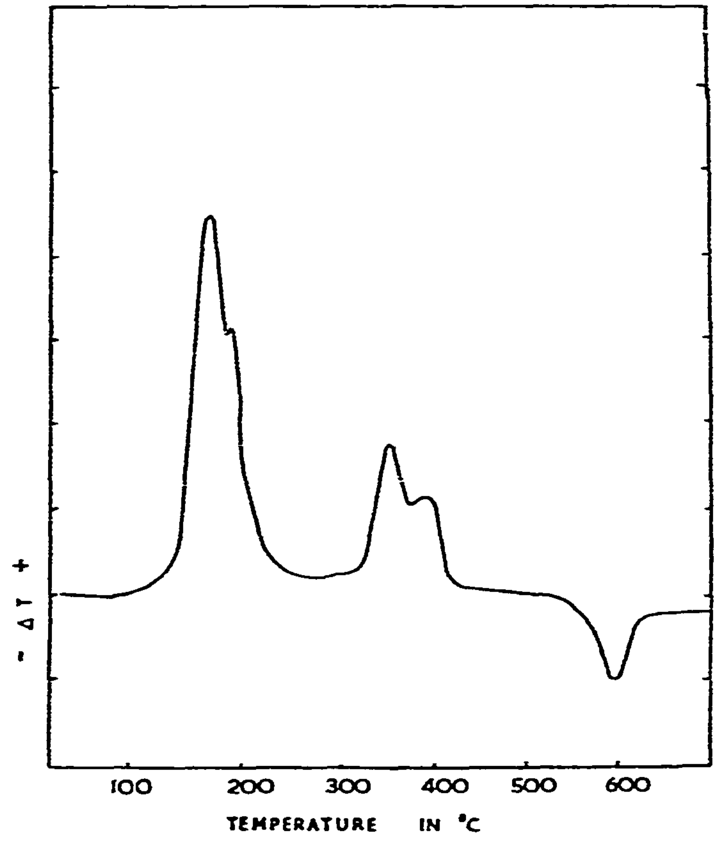

Fig. 2. DTA curve of $In(OH)_3 + H_3BO_3$.

Exothermic reaction peaks were observed for all four mixtures (Figs. 1–4). These exothermic peaks are considered to be the result of the rapid evolution of heat caused by the formation of the respective borates. These exotherms were at 736, 620 and 600 °C, for the reactions with scandium, yttrium and indium, respectively, while with lanthanum (Fig. 4) there was an exotherm with three peaks between 630 and 760 °C. These must be associated with the fact that $LaBO_3$ has the aragonite structure while the others are of the calcite type. It is known that if a polymorphic compound is heated, a series of transitions occurs from aragonite to calcite[3]. It is suggested that the reverse is true for the formation of a polymorphic compound and is responsible for the additional exotherms.

The TG data supported the results obtained on the DTA except that the calculated loss of water was slightly higher than the experimentally obtained values.

The *d*-spacings of the DTA and TG residues were similar to those obtained by heating these oxides for several hours at 1000 °C. These results were identical to those of Goldschmidt and Hauptmann[1] who showed the compounds to be the borates of scandium, yttrium, lanthanum and indium.

Since the *d*-spacings of the unheated and heated mixtures of oxide and boric acid were found to be entirely different from one another, and since several lines were common in each of the unheated mixtures and absent from all of the heated mixtures, it was decided that these lines were originally due to boric acid in the mixtures and

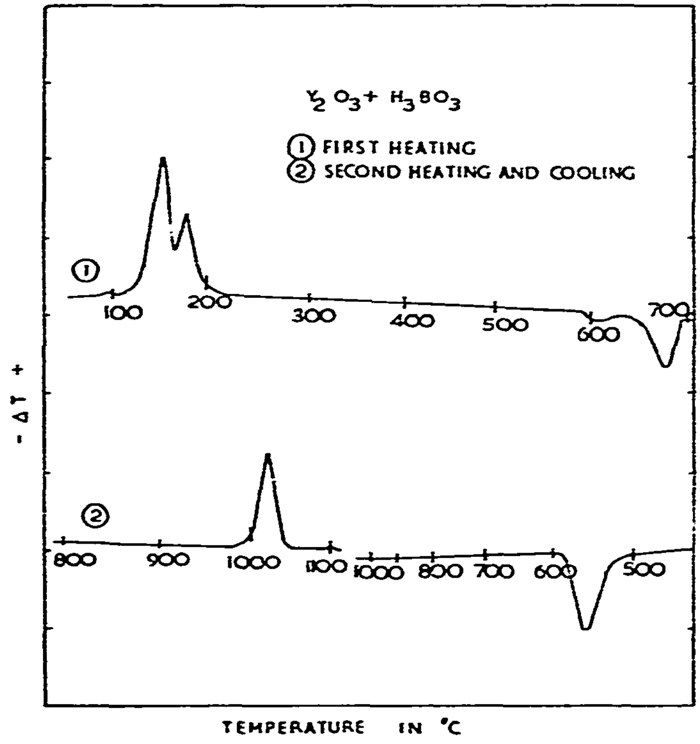

Fig. 3. DTA curve of $Y_2O_3 + H_3BO_3$.

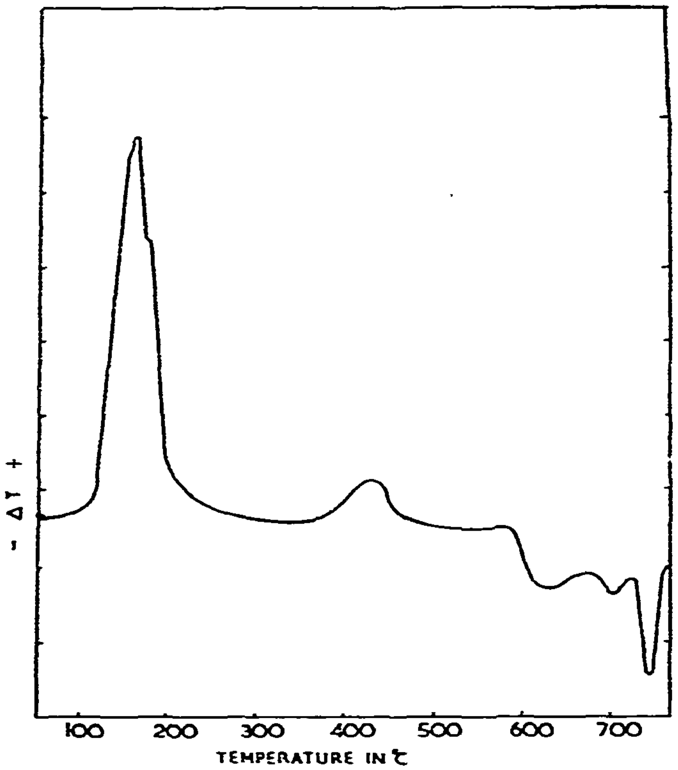

Fig. 4. DTA curve of $La_2O_3+H_3BO_3$.

that the final product contained no boric acid. The *d*-spacings of the oxides coincided with the values found in ref. 4.

Unlike the previous workers[1] who heated $Sc_2O_3+H_3BO_3$, $Y_2O_3+BO_3$, $La_2O_3+H_3BO_3$, and $In(OH)_3+H_3BO_3$ for 94, 84, 84 and 93 h at 1000 °C, respectively, it was found that the *d*-spacings of the borate heated for 3 h were similar to the *d*-spacings of the samples heated for 8 h at 1000 °C. The residues remaining after DTA and TG analyses also gave a similar diffraction pattern. Generally speaking, however, the borates studied were thermally stable within the temperature range used in the DTA and TG analyses.

DISCUSSION OF YBO_3

The DTA of YBO_3 gave an endothermic reaction peak at 1020 °C in the heating curve and an exothermic reaction peak at 580 °C in the cooling curve. These two curves were of approximately the same area and gave a calculated energy of approximately 21 kJ mol^{-1} and -21 kJ mol^{-1} for these reactions (Tables 2 and 3). The result obtained by Mr. Francois Brisse at the N.S. Technical College was identical.

The TG showed no gain or loss of weight at corresponding temperatures, and TMA showed that the sample did not melt (Table 4). It is therefore quite clear that

TABLE 2

DTA RESULT FROM A SAMPLE OF YBO_3

(a) = prepared by heating ($Y_2O_3+H_3BO_3$) at 1000°C for 21 h; (b) = heated at 1000°C for 8 h; (c) = heated under pressure for 19 h. (H) in heating and (C) in cooling curves. The heats of reaction are given in kJ mol^{-1}.

Run	*Peak temp.* (°C)	*Area* (H)	Δ*H* (H)	*Peak temp.* (°C)	*Area* (C)	Δ*H* (C)	*Cooling rate*
1st	1020	0.65	20.88	580	0.65	−20.88 (a)	
2nd	1020	0.65	20.88	580	0.65	−21.00 (a)	
	1020		20.88	580		−20.92 (b)	
1st	1020		20.88	580		−21.00 (c)	very slowly
2nd	1020		21.04	680		−21.42 (c)	several times 700–1100°C
3rd	1020		20.88	580		−21.09 (c)	as usual
4th	1020		20.88	580		−21.76 (c)	slowly six times 700–1300°C

TABLE 3

DTA RESULT OF $Y_2O_3+H_3BO_3$

Run	*Peak temp.*[a] (°C)	*Area* (H)	*Gain*	*Peak temp.*[a] (°C)	*Area* (C)	*Cooling rate* (°C min^{-1})
1st	173, 185	1.50, 3.96				usual
	620[a]		10			
2nd	1021	0.69	10	580	0.69	7
3rd	1020	0.62	6	580	0.62	6.6
4th	1020	0.62	6	580	0.62	14
5th	1020	0.62	6	580	0.62	14
6th		Heating between room temperature and 880°C → no reaction				

[a] Exotherm.

the DTA peaks are due to the change in energy accompanying a solid state transition. The X-ray diffraction patterns of the original sample and final residues were identical. It follows therefore, that this compound exhibits a "displacive" type transition with considerable hysteresis.

A "displacive" transformation indicates that the high temperature form of a polymorph is always the open form with a larger specific volume, larger specific heat, higher entropy and higher symmetry[5]. The down-temperature transformation usually results in twins.

It has been shown[1] that the low temperature crystalline structure of YBO_3 is the calcite structure. Calculations of the lattice constants from the diffraction pattern

TABLE 4

TMA RESULT OF YBO_3

The sample was heated between quartz plates with a magnification of 50:1.

Temp. (°C) (heating)	*Area*[a] × 10^2	*Temp. (°C) (cooling)*	*Area*[a] × 10^2
RT	9.08	RT	9.04
100	9.10	100	9.06
200	9.14	200	9.08
300	9.14	300	9.10
400	9.14	400	9.13
500	9.16	500	9.13
600	9.20	600	9.18
700	9.20	700	9.19
800	9.22	800	9.20
900	9.25	900	9.24
1020	9.26	1020	9.26

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[a] Accuracy of these results is of the order of ±3%. The increase in area from RT to 1020°C is approximately 2% and the decrease from 1020°C to RT is approximately 2.4%.

TABLE 5

X-RAY DIFFRACTION PATTERN OF YBO_3

RT		*800 °C (rising temp)*		*1000 °C*		*800 °C*[a]	
d(Å)	*I*	*d(Å)*	*I*	*d(Å)*	*I*	*d(Å)*	*I*
4.459	6	6.345	6	4.360	7	4.550	6
3.300	8	5.228	4	4.169	8	4.351	4
3.098	2	3.088	10	3.592	10	4.188	10
2.635	10	2.665	8	3.307	4	3.402	10
2.215	3	2.503	4	3.141	3	3.181	3
1.898	8	1.897	8	2.758	9	3.013	2
1.830	10	1.620	6	2.565	9	2.720	10
1.744	8	1.599	6	2.164	2	2.576	4
1.646	3			2.072	8	2.280	4
1.536	5			1.876	6	1.959	8
1.438	3			1.844	7	1.884	10
1.343	4			1.663	8	1.797	9
1.318	4			1.484	5	1.698	4
1.228	3					1.490	5
1.194	6						

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[a] After being heated for 15 minutes above 1000 °C.

TABLE 6

X-RAY DIFFRACTION PATTERN DATA FOR Y, 0.8; La, 0.2; BO$_3$, 1.0 AT 400°C

(M) = after heating the mixture at 860°C; and (Y) = after heating YBO$_3$ at 1000°C.

I (M)	*d* (*Å*) (M)	*I* (Y)	*d* (*Å*) (Y)
6	4.284	7	4.320
8	4.107	8	4.140
wk	3.963	10	3.598
4	3.700	wk	3.340
10	3.571	wk	3.164
4	3.322	v wk	2.961
2	3.080	8	2.805
wk	2.937	9	2.596
8	2.751	v wk	2.190
2	2.674	8	2.105
4	2.535	v wk	2.004
wk	2.468	6	1.897
v wk	2.206	7	1.868
wk	2.136	v wk	1.790
8	2.069	8	1.686
6	1.868	v wk	1.636
6	1.845	v wk	1.545
wk	1.800	wk	1.501
wk	1.771		
v wk	1.723		
v wk	1.662		

data obtained at 1020°C tend to show the pseudo-hexagonal configuration similar to the vaterite structure [6]of CaCO$_3$. This structure is not definitely established since some lines are missing from the diffraction pattern. A couple of the lines are also quite close to those expected for a cubic structure (Tables 5 and 6). These transitions are so rapid that the high temperature form cannot be retained by quenching. The introduction of LaBO$_3$ (aragonite structure) in the YBO$_3$ lattice caused the transition temperatures to be lowered to 680 and 240°C, respectively (Tables 7–9). This clearly suggests that solid solutions existed between both species and that LaBO$_3$ is more soluble in the high temperature form of YBO$_3$. Theoretically the introduction of new ions into the lattice alters the cohesive force and the lattice energy[5]. The X-ray diffraction patterns of the heated mixtures indicated that a transformation into the low temperature calcite form had occurred. The stabilization of the high temperature open form by the compact aragonite (Table 6) to produce the calcite structure strongly suggests that the high temperature structure of YBO$_3$ is the structure which resembles the vaterite structure in CaCO$_3$. The diffraction patterns showed an increase in the calcite lattice which is expected considering the bigger size of La^{3+} compared to that of Y^{3+}. The specific volumes of aragonite, calcite and vaterite (CaCO$_3$) are 0.346, 0.3698 and 0.394 cm^3 g^{-1}, respectively. The average value for the aragonite and vaterite is 0.370 as compared to 0.3698 cm^3 g^{-1} for calcite.

TABLE 7

DTA RESULT OF Y, 0.8; La, 0.2; BO_3, 1.0

Run	*Peak temp. (°C)*	ΔH_{YBO_3}[a] (H)	*Peak temp. (°C)*	ΔH[a] (C) (*kJ mol*$^{-1}$)
1st	670	12.59	240	−9.87
2nd	680	11.46	240	−9.41
3rd	680	9.87	240	−8.58

[a] ΔH calculated on the amount of YBO_3 in the original intake.

TABLE 8

DTA RESULT OF Y, 0.5; La, 0.5; BO_3, 1.0

Run	*Peak temp. (°C)*	ΔH[a] (H)	*Peak temp. (°C)*	ΔH[a] (C)
1st	700, 1040 1210	20.96; 1.78 4.90	1020 240	−4.48; −14.69
2nd	680, 1060 1200 1020[b]	11.21; 2.29 7.91	240	−6.49 −6.49
3rd	690 1180[b]	4.73	240	−10.17
4th	690	4.27	Air quenched	
5th	700	5.10	Air quenched	

[a] ΔH calculated on the amount of YBO_3. [b] Ill-defined, small and rounded curves.

TABLE 9

DTA RESULT OF Y, 02; La, 0.8; BO_3, 1.0

Run	*Peak temp. (°C)*	*Area* (H)	ΔH_H (*kJ*)	*Peak temp. (°C)*	*Area* (C)	ΔH[a] (C) (*kJ mol*$^{-1}$)
1st	690	0.15	9.62	315	0.15	−9.62
2nd	690	0.12	7.70	300	0.10	−6.40
3rd	680	Negligible		290	Negligible	

[a] ΔH calculated on the amount of YBO_3. [b] In the original intake.

It is concluded that YBO_3 is dimorphic and the reversible transitions occur with considerable hysteresis. Each transition occurred abruptly. The thermal energy necessary for these transformations is -21 kJ mol^{-1}. Introduction of La^{3+} ions stabilizes the low temperature form, but is soluble in the high temperature form. The high temperature form resembles the pseudo-hexagonal vaterite structure found in $CaCO_3$. A mixture with less than 20 mol % of $LaBO_3$ showed complete solution of the pseudohexagonal structure.

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