

PHASE-TRANSFORMATION OF BORAX DURING THERMAL TREATMENTS

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In recent years different problems on sodium diborate have been worked out by a number of workers. It is well established from their study that the decahydrate of sodium diborate or borax belongs to the monoclinic crystal class with the axial parameters as $a = 11.82 \pm 0.04 \text{ \AA}$, $b = 10.61 \pm 0.03 \text{ \AA}$, $c = 12.30 \pm 0.04 \text{ \AA}$ and $\beta = 106.35^\circ \pm 0.4$. Except the decahydrate and anhydrous sodium diborate, other different hydrates of borax, such as pentahydrate, tetrahydrate, dihydrate and monohydrate, are known to exist. McIntosh and Mathews (1948), Menzel and Schulze (1940), and Minder (1935) obtained valuable informations so far as the problems on sodium diborate were concerned. In the present investigation an attempt has been made to obtain full information regarding the phase-transformation of borax decahydrate purely from the X-ray crystallographic point of view and, along with that, investigations into the structural details of some of the transformed products have been carried out by X-ray method.

EXPERIMENTAL

At the first stage, a preliminary differential thermal analysis of decahydrate of sodium diborate was made so as to know the temperature zone where its structural change occurs. The experimental arrangement was the same as what was used by us (1955) in the case of anhydrous Na_2SO_4 . The differential thermal curve obtained is shown in Fig. 1. It can be easily seen that an exothermic peak occurs at 50°C . and three endothermic peaks occur near 75°C ., 162°C ., and 202.5°C . Thus we got some idea about the transformation temperatures of different phases of borax within 300°C . In keeping with that information borax powder was heated at different temperatures up to 750°C . for 12 to 16 hours in an electric furnace till a constant weight was obtained in each case. Thus a number of samples of different thermal history was obtained.

X-RAY STUDY

X-ray photograph of each specimen, enclosed in a very thin-walled, capillary glass tube sealed at both ends, was taken in a cylindrical camera with $\text{Cu-K}\alpha$ radiations. X-ray pictures are given below and X-ray data are shown in Tables II, III, IV and V. The crystalline component in each specimen is identified by comparison of the X-ray data of that specimen with the published data of different varieties of $\text{Na}_2\text{B}_4\text{O}_7$, both hydrous and anhydrous. In that connection, it is worth while to mention that during the process of dehydration of decahydrate of $\text{Na}_2\text{B}_4\text{O}_7$, tetrahydrate of $\text{Na}_2\text{B}_4\text{O}_7$ is not obtained as has also been observed by many previous workers.

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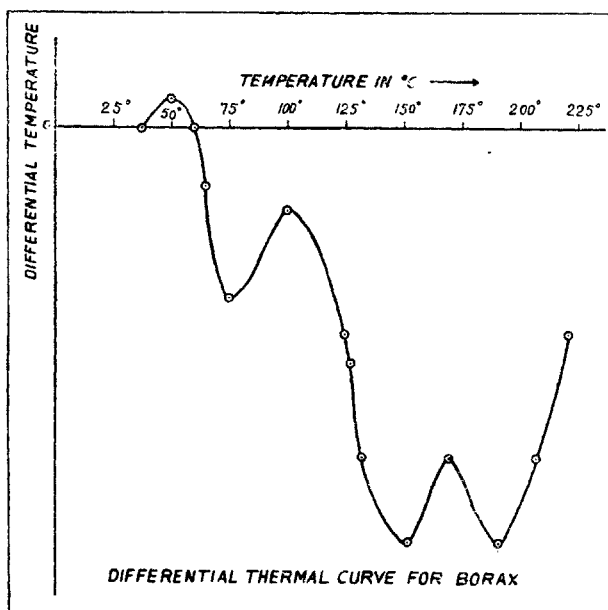


FIG. 1.

The nature of the X-ray picture depends on the thermal history of the specimen. Again, the analysis of the diffraction pattern of different specimens reveals some interesting informations. The decahydrate transforms into pentahydrate above 50°C. and this transition was recorded in the differential thermal analysis. The X-ray picture of borax heated 60°C. clearly shows that the decahydrate has been transformed into pentahydrate. It is also observed that in the X-ray picture of the specimens which have been dehydrated at a still higher temperature there is an indication of a diffuse band.

AMORPHOUS PHASE

As a matter of fact, the X-ray picture of the specimens dehydrated at 320°C. and 350°C. reveals bands. It is found that after the disintegration of pentahydrate, only diffuse bands come in the picture and with the further rise in temperature to about 450°C. the bands become more prominent. The Bragg angles for the centres of the bands, as calculated from the picture, are 10° 1' (m), 15° 25' (m.s.), 22° 35' (w), which can be satisfactorily compared with those of the strongest lines of pentahydrate. The differential thermal analysis of borax shows that there are two transitions at 150°C. and 200°C. The X-ray diffraction patterns of the samples heated at 150°C. and 200°C. show a slight departure from the usual X-ray photograph of pentahydrate. In both the pictures evidences of an amorphous phase along with a crystalline phase are found. But the spacings of the bands in these pictures are almost equal to those of the strongest lines of the pentahydrate. The main difference between the two pictures of borax treated at 150°C. and 200°C. lies in the fact that the number of powder lines in the high temperature treated product increases. It is interesting to note that when X-ray diffraction pattern of the sample heated at 200°C. is taken after about seven days of heating no bands can be seen in the picture and the X-ray diffraction pattern is similar to that of the sample heated at 60°C.

TABLE I

Diffraction angles of some varieties of sodium diborate

(After Hanawalt, Rinn and Fravel (1938), the corresponding Bragg angles have been calculated here for the respective spacings)

Decahydrate		Pentahydrate	
θ	Intensity	θ	Intensity
4° 51'	0.07	7° 54'	0.13
5° 31'	0.07	9° 23'	0.13
6° 13'	0.13	10° 5'	0.60
7° 46'	0.20	12° 56'	0.53
8° 31'	0.13	14° 55'	0.20
9° 7'	0.47	15° 11'	1.00
9° 58'	0.07	16° 12'	0.13
11° 13'	0.40	17° 13'	0.33
12° 19'	0.07	18° 43'	0.60
15° 1'	0.20	19° 55'	0.13
15° 44'	0.53	20° 36'	0.67
17° 26'	1.00	22° 31'	0.33
18° 14'	0.07	23° 23'	0.27
19° 13'	0.20	24° 44'	0.13
20° 29'	0.07	25° 19'	0.40
21° 5'	0.07	27° 49'	0.70
21° 43'	0.07	29° 35'	0.13
22° 24'	0.07	31° 0'	0.07
23° 16'	0.07	32° 4'	0.07
23° 54'	0.13	33° 6'	0.07
24° 36'	0.13		
25° 38'	0.07		
26° 6'	0.10		
26° 56'	0.10		
27° 49'	0.10		
28° 34'	0.07		

TABLE II

Bragg angles, intensity and spacings of the X-ray diffraction patterns of borax heated to 60°C.

θ	Intensity	d in Å
5°	s	8.835
6° 12'	w	7.131
7° 52'	m	5.565
10° 8'	v.s.	4.375
12° 57'	m.s.	3.436
15° 8'	v.s.	2.949
17° 10'	m	2.609
18° 40'	w	2.406
19° 54'	m	2.268
20° 40'	s	2.182
23° 26'	m	1.936
24° 45'	w	1.840
25° 22'	m	1.797

It is to be noted here that McIntosh and Mathews (1948) mentioned that X-ray picture of the specimens dehydrated at 100°C. reveals no Debye-Scherrer lines in the picture. The similar results were obtained by us when the specimen was dehydrated in the temperature lying between 320°C. to 450°C., but not at 100°C.

TABLE III

Bragg angles, intensity and spacings of the X-ray diffraction patterns of borax heated to 150°C.

θ	Intensity	d in Å
5° 10'	s (band)	8.559
10° 1'	s (band)	4.427
17° 57'	w	2.499
19° 9'	w	2.347
23° 48'	w (band)	1.908
30° 32'	w	1.516
32° 57'	w	1.415

TABLE IV

Bragg angles, intensity and spacings of the X-ray diffraction patterns of borax heated to 200°C.

θ	Intensity	d in Å
4° 49'	m.s. (band)	9.168
10° 5'	m.s. (band)	4.399
10° 5'	s. (sharp line)	4.339
12° 36'	v.w.	3.530
15° 1'	m.s.	2.972
16° 55'	v.w.	2.646
20° 21'	v.w.	2.215
21° 55'	v.w.	2.063
25° 53'	v.w.	1.764

During the course of the present investigation, it was observed that the relation between the X-ray pattern of a heat-treated specimen with its percentage chemical composition is not very satisfactory. As for example, we can cite the percentage chemical composition of the specimen which has been dehydrated at 300°C. is different from that required for pentahydrate, yet the X-ray diffraction gives only the lines of pentahydrate. The apparent explanation for this is that some portion of the water has remained as absorbed water, which enters the pores and capillaries between the crystallite boundaries, thereby taking no part in the structural distribution. With the further rise of temperature, this absorbed water comes out, maintaining the original structure.

ANHYDROUS BORAX

In course of present observation it is found that in the temperature zone of 675°C., there is an abrupt crystallization from the amorphous phase and from the chemical composition of that specimen it is identified as anhydrous $\text{Na}_2\text{B}_4\text{O}_7$ and at 720°C. it transforms into anhydrous borax glass.

We confine our investigations for the present to the above anhydrous borax obtained by the dehydration process. The structural details of that specimen are obtained by the application of Lipson's (1948) method to the data of the powder pattern of that specimen. The speciality of the above method lies in the fact that this method of crystal-structure analysis can be uniquely applied to the powder pattern of orthorhombic crystal class where other existing method fails.

Table V gives the $\text{Sin}^2\theta$ values, spacings of the powder lines of experimental borax.

TABLE V

Application of Lipson's method in the determination of the crystal class of the crystalline component of borax formed during heating at 675°C.

	$\text{Sin}^2\theta$	d in Å	V.I.
5° 4'	0.0078	8.730	m
6° 46'	0.0138	6.533	s
7° 40'	0.0178	5.772	v.w.
8° 26'	0.0216	5.250	s
9° 12'	0.0256	4.816	v.w.
10° 15'	0.0316	4.328	s
11° 25'	0.0392	3.890	s
12° 52'	0.0494	3.457	m
13° 37'	0.0554	3.271	w
14° 32'	0.0630	3.068	w
15° 3'	0.0678	2.966	w
15° 52'	0.0747	2.816	m
16° 51'	0.0840	2.658	m
17° 32'	0.0908	2.557	w
18° 38'	0.1018	2.410	m.w.
21° 4'	0.1293	2.142	m
22° 15'	0.1432	2.036	m
23° 34'	0.1598	1.926	m
24° 13'	0.1680	1.877	w
25° 18'	0.1813	1.802	w
26° 32'	0.1986	1.724	v.w.

TABLE VI

Differences of the $\text{Sin}^2\theta$ values

$\text{Sin}^2\theta$	-a	-b	-c	-d	-e	-f	-g	-h
a	0.0078							
b	0.0138	0.0060						
c	0.0178	0.0100	0.0040					
d	0.0216	0.0138	0.0078	0.0038				
e	0.0256	0.0178	0.0118	0.0078	0.0040			
f	0.0316	0.0238	0.0178	0.0138	0.0100	0.0060		
g	0.0392	0.0314	0.0254	0.0214	0.0176	0.0136	0.0076	
h	0.0494	0.0416	0.0356	0.0316	0.0278	0.0238	0.0178	0.0102
i	0.0554	0.0476	0.0416	0.0376	0.0338	0.0298	0.0238	0.0162
j	0.0630	0.0552	0.0492	0.0452	0.0414	0.0374	0.0314	0.0238
k	0.0678	0.0596	0.0536	0.0496	0.0458	0.0418	0.0358	0.0282
l	0.0747	0.0669	0.0609	0.0569	0.0531	0.0491	0.0431	0.0355
m	0.0840	0.0762	0.0702	0.0662	0.0624	0.0584	0.0524	0.0448
n	0.0908	0.0830	0.0770	0.0730	0.0692	0.0652	0.0592	0.0516
o	0.1018	0.0940	0.0880	0.0840	0.0802	0.0762	0.0702	0.0626

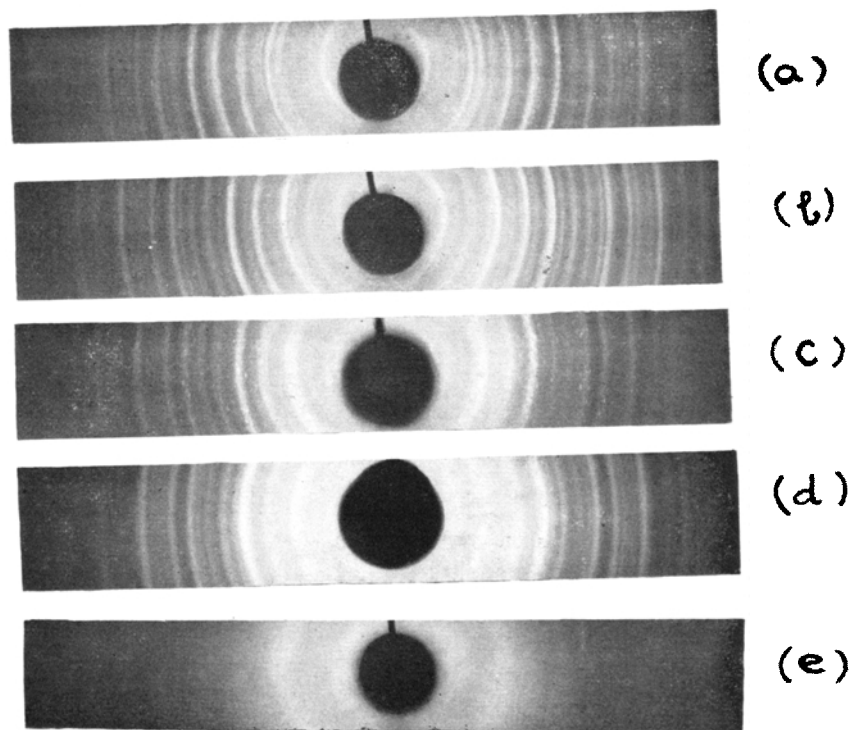


FIG. 2. Powder diffraction patterns of borax: (a) borax, (b) heated to 60°C., (c) heated to 100°C., (d) heated to 120°C., (e) heated to 150°C. (camera radius $r = 3.89$ cm.).

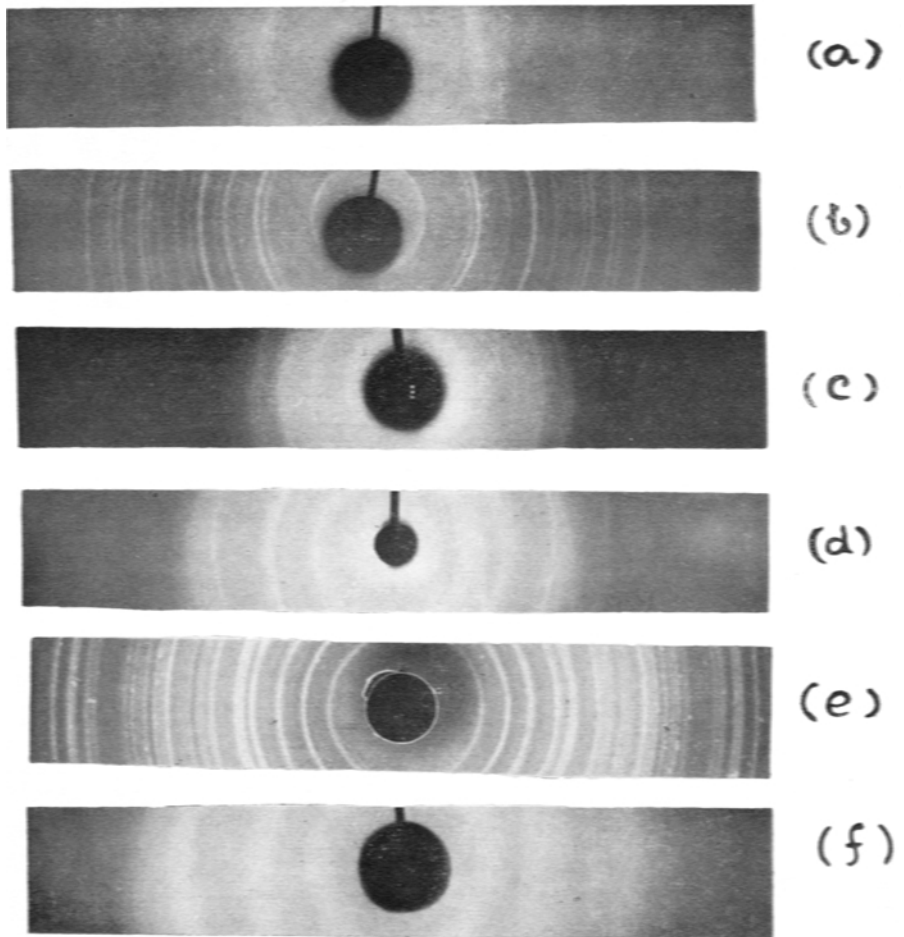


FIG. 3. Powder diffraction pattern of borax: (a) heated to 200°C ., (b) heated to 200°C . and kept at room temperature for seven days, (c) heated to 311°C ., (d) heated to 450°C ., (e) heated to 675°C ., (f) borax glass (camera radius $r = 3.89$ cm. for (a) to (c), $r = 2.83$ cm. for (d), $r = 5.73$ cm. for (e), $r = 3.89$ cm. for (f)).

TABLE VI—contd.
Differences of the $\text{Sin}\theta$ values

$\text{Sin}\theta$	-i	-j	-k	-l	-m	-n	-o	-p	-q	-r	-s	-t
j	0-0076											
k	0-0074	0-0044										
l	0-0193	0-0117	0-0073									
m	0-0286	0-0210	0-0166	0-0093								
n	0-0354	0-0278	0-0234	0-0161	0-0068							
o	0-0464	0-0388	0-0344	0-0271	0-0178	0-0110						
p	0-0739	0-0663	0-0619	0-0546	0-0453	0-0385	0-0275					
q	0-1432	0-0802	0-0758	0-0685	0-0592	0-0524	0-0414	0-0139				
r	0-1598	0-0968	0-0914	0-0861	0-0758	0-0690	0-0580	0-0305	0-0166			
s	0-1680	0-1126	0-1006	0-0933	0-0840	0-0772	0-0662	0-0387	0-0248	0-0082		
t	0-1813	0-1256	0-1136	0-1066	0-0973	0-0905	0-0795	0-0520	0-0381	0-0215	0-0133	
u	0-1936	0-1432	0-1312	0-1239	0-1146	0-1078	0-0968	0-0693	0-0554	0-0388	0-0306	0-0073

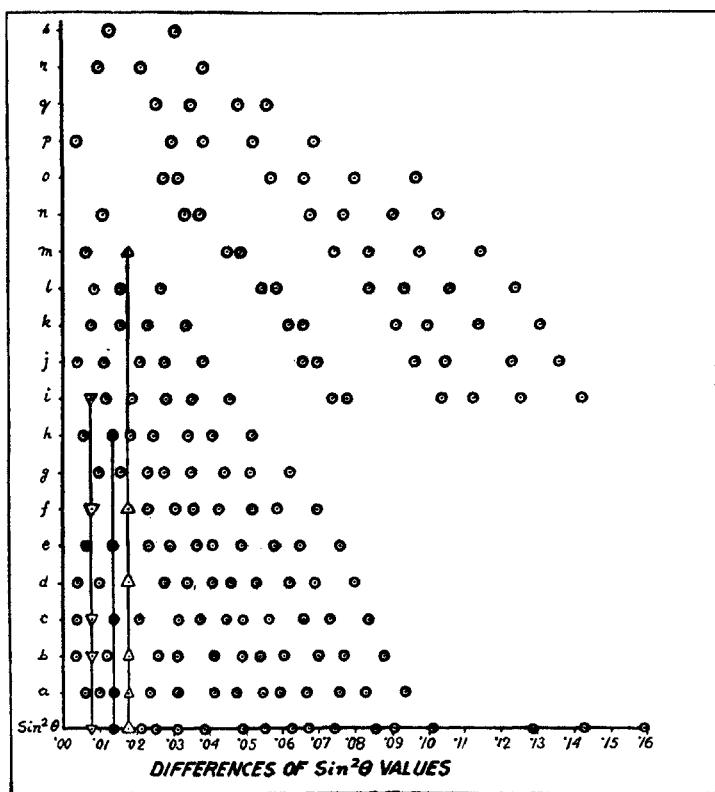


FIG. 4

From Table V it is seen that there are only 21 lines with $\text{Sin}\theta$ less than 0.5. Thus, by the help of the equation $A \sim 0.4 \text{ Sin}^2\theta / M^{\frac{1}{3}}$ (Lipson, 1948), we can expect A, B or C to be of the order of $0.4 \times 0.25 / (21)^{\frac{1}{3}} = 0.0131$.

Table VI gives all the $\text{Sin}^2\theta$ values in the first vertical column; in the subsequent columns are given the differences between all the $\text{Sin}^2\theta$ values written in the first column and the particular $\text{Sin}^2\theta$ values as designated at the head of each vertical column.

From Fig. 4 it will be observed that when the vertical lines are drawn, the lines are seen to pass through the points 0.0078, 0.0138 and 0.0178 for 5, 5 and 6 times respectively. One of this constant 0.0138 was found to be very near to that found by the help of the equation. Taking these constants as A, B and C, it was seen that if the value 0.0178 be quarted, then all the lines of the powder pattern can be indexed easily. Thus, with $A = 0.0138$, $B = 0.0078$ and $C = 0.00445$, the anhydrous borax crystal was found to have orthorhombic symmetry with $a = 6.533 \text{ \AA}$, $b = 8.730 \text{ \AA}$ and $c = 11.54 \text{ \AA}$ respectively. Table VII shows the comparison of the values observed and calculated from the unit cell dimensions and the $h k l$ values for all the powder lines.

The axial lengths $a = 6.533 \text{ \AA}$, $b = 8.730 \text{ \AA}$ and $c = 11.54 \text{ \AA}$ for the anhydrous borax formed at 675°C . with a density 2.1 gms./cm.^3 allow only 4 molecules in the unit cell. From Table VII, it can be seen that there is no systematic absence in any order of reflections, except for the 001 plane where $l \neq 2n$. The number of reflecting planes in the case of a powder diffraction being limited, it is very difficult to assign

TABLE VII

*Comparison of the observed and calculated $\text{Sin}^2\theta$ values
and the indices of the powder lines*

$\text{Sin}^2\theta$ obs.	h k l	$\text{Sin}^2\theta$ cal.
	010	0-0078
0-0078	100	0-0138
0-0138		
0-0178	002	0-0178
0-0216	110	0-0216
0-0256	012	0-0256
0-0316	102 } 020 }	0-0316 0-0312
0-0392	112	0-0394
0-0494	121 } 022 }	0-0494
0-0554	200	0-0552
0-0630	210 } 122 }	0-0630
0-0674	211	0-0674
0-0747	031	0-0746
0-0840	130	0-0840
0-0908	221	0-0908
0-1018	132	0-1018
0-1293	041	0-1293
0-1432	141	0-1431
0-1598	321 or 006	0-1598
0-1680	016	0-1680
0-1813	035	0-1814
0-1986	331	0-1988

any definite space-group in this case. But from the above condition it seems that the most suitable space-group for experimental borax is D_2^2 or $P/222_1$.

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SUMMARY

The complete phase-transformation of borax during thermal treatments was studied from X-ray crystallographic point of view. The most interesting thing that was noted in the present investigation was that there was an abrupt crystallization of the amorphous phase in the temperature zone of 675°C. The chemical composition of that specimen indicated it to be anhydrous $\text{Na}_2\text{B}_4\text{O}_7$. The structural details of the above products were found out by the application of the method suggested by Lipson. This crystalline variety of anhydrous borax was found to have an orthorhombic symmetry with the axial parameters as $a = 6.468 \text{ \AA}$, $b = 8.270 \text{ \AA}$ and $c = 11.54 \text{ \AA}$. The density of the anhydrous borax, together with the above cell dimension,

allowed only 4 molecules in the unit cell. There was no systematic absence of any kind of reflections except for $l \neq 2n$ in the X-ray diffraction pattern, which showed the most suitable space-group for anhydrous borax to be $D_2^2_1$ or $P/222_1$.

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