pure state. The oxide of valence 1 was formed in the reduction of the perrhenate in dilute hydrochloric acid with zinc and that of valence 2 with cadmium. Both lower oxides are black in color, insoluble in hydrochloric acid, and not readily attacked by dilute alkaline chromate nor acid ferric sulfate, and not by concentrated solutions of alkali. They are dissolved by nitric acid and by bromine water.

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A Crystalline Boric Oxide

BY L. McCULLOCH

This paper announces the discovery by chance of a crystalline boric oxide. Until recently boric oxide has been known as a glass which has resisted efforts to cause it to crystallize.

Taylor and Cole[1] have reported a crystalline oxide made by heating boric acid below 225° in vacuum, having the form of opaque pseudomorphs of the boric acid crystals. From its X-ray pattern they judged their product to be crystalline, and from its quiet fusion they believed it to be anhydrous. They placed its melting point at 294°, and its density at 1.805.

Morey and Merwin[2] were unable to duplicate these results. They also attempted to cause boric oxide to crystallize by aid of " 'mineralizers' other than water," and concluded that "the crystallization of boric oxide is yet to be proved."

More recently, von Stackelberg, Quatram and Dressel[3] have contributed a diagram of the system B_2O_3–H_2O, and a study of the vapor phase. They found only the crystalline solids H_3BO_3 and HBO_2, and a glassy liquid of variable water content.

The attempts at preparation of a crystalline oxide were made with the intentional exclusion of water. It was not anticipated that a crystalline oxide would separate from an aqueous liquid.

This reaction was discovered while the writer was working with boric acid fused in loosely covered quart "tin cans" under atmospheric pressure and kept in an oven between 225 and 250°. Under these conditions the escape of water vapor was retarded and the liquids contained from 8 to 15% water. Occasionally the fused acids were stirred. The boric acid was not of high purity, but was of a good technical grade. It was found that the liquid did not remain clear indefinitely, but after a period of days it became clouded, then in a few hours it thickened and became pasty, and reached finally the state of a stone-like solid. Its combined water had escaped, and from its opaque whiteness the substance was considered to be finely crystalline in structure. In one experiment this reaction acquired "volcanic violence," bubbling out steam and filling the air with white fumes.

Later experiments showed that after prolonged periods of time, boric acid also in glass bottles and in Pyrex flasks would crystallize spontaneously. Impurities seem to shorten the "induction period." A boric acid of "technical" grade became crystalline in seven days, while one of "chemical purity" took fourteen days (fifty-gram samples in Pyrex bulbs at 225°). The first crystals appear as small spheroids (0.3 mm. diameter) upon the glass walls.

By the addition of "seed" from crystalline oxide previously obtained, boric acid fusions can be induced to crystallize immediately. By this method the oxide can be prepared in large quantities. The oxide so prepared is a white, stony substance, with a coarse foam-structure left by the escape of steam. It is so hard and strong that it can only with difficulty be shattered by a hammer. The hardness on the scale of minerals is about 4.

The density is 2.42, by weighing in transformer oil after removal of air in vacuum. The density of boric oxide glass is given as 1.84. This is a remarkable shrinkage in volume on crystallization.

The composition was found by the simple method of analysis given below to be essentially anhydrous boric oxide. One of the products analyzed was a solid cake (1000 g.) from a loosely covered "tin can" of "seeded" boric acid which had been held at 250° for three days. A fragment of this weighing 16.22 g. yielded 28.62 g. H_3BO_3; another weighing 6.48 g. yielded 11.43 g. Hence the analyses give 99.36 and 99.33% B_2O_3. There is one molecule of water to at least 50 molecules of boric oxide. Such an amount might be held in films within a mass of very minute boric oxide crystals.

The melting point is between 460 and 470° for another specimen found after fusion in a sealed glass tube to contain 99.6% B_2O_3. These crystalline granules (10 g. from chemically pure boric acid, crystallized in Pyrex glass) had been sealed within a Pyrex bulb under high vacuum after baking to 400°. The change of the granules to the glassy state was detected easily by observing the sintering and the acquired transparency. That there had been actual fusion was borne out also by tests of the power of

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[1] N. W. Taylor and S. S. Cole, THIS JOURNAL, **56**, 1648 (1934); *J. Am. Ceramic Soc.*, **18**, 55–61 (1935).

[2] G. W. Morey and H. E. Merwin, THIS JOURNAL, **58**, 2248–2254 (1936).

[3] M. von Stackelberg, F. Quatram and Jutta Dressel, *Z. Elektrochem.*, **43**, 14–28 (1937).

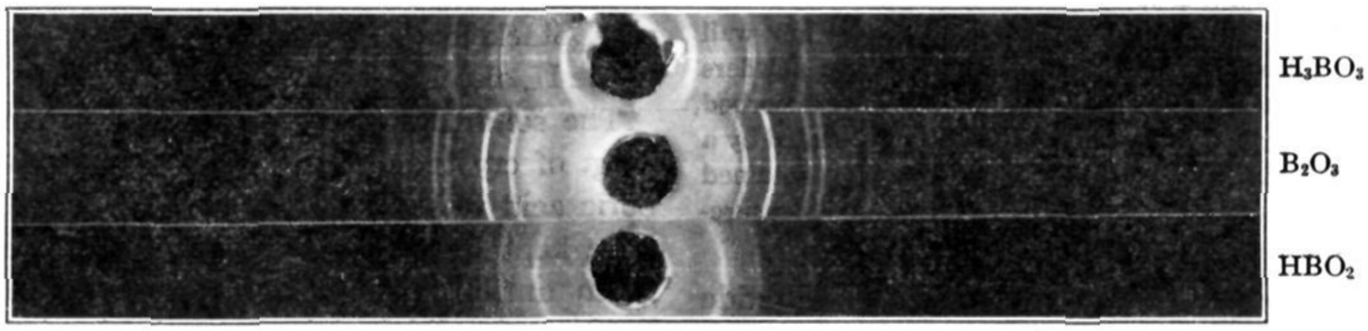

Fig. 1.

several specimens to "seed" or to induce crystallization in fused boric acid. One which had become glassy at 460–470° had lost this power, whereas another retained it although it had been held for three days at 450–460°.

The crystalline nature of the new oxide is supported by the sharp lines of its X-ray pattern, shown in Fig. 1, which do not correspond with the lines of H_3BO_3 and of HBO_2 shown for comparison. The metaboric acid, HBO_2, was prepared by heating H_3BO_3 at 125° for eighteen hours.

TABLE I

X-RAY DIFFRACTION ANGLES

Line no.	Intensity	Separation, mm. (corr.)	Diffraction angles, degrees
	CRYSTALLINE B_2O_3		
1	VS	25.8	12.9
2	VW	28.5	14.2
3	VVS	32.0	16.0
4	VVW	33.6	16.8
5	VVW	36.4	18.2
6	VVW	38.6	19.3
7	VS	39.8	19.9
8	VW	41.7	20.8
9	VS	42.9	21.5
10	W	47.2	23.6
11	W	49.9	25.0
12	S	53.5	26.7
13	W	59.2	29.6
14	W	60.5	30.2
15	VVW	60.9	30.5
16	S	67.2	33.6
17	VVW	70.1	35.0
18	VVW	71.3	35.6
19	VVW	72.6	36.3
20	VVW	76.3	38.2
21	W	80.1	40.0
22	W	82.0	41.0
23	W	85.1	42.5
24	VVW	86.9	43.5
25	W	90.7	45.4
26	VVW	94.6	47.3
27	W	96.4	48.2
28	W	99.7	49.8
29	W	101.4	50.7
30	W	104.2	52.1
31	VVW	109.7	54.8
32	W	111.4	55.7
33	VVW	114.9	57.5
34	VW	126.1	62.0
35	VW	128.2	64.1
36	W	131.8	65.9
37	W	140.8	70.4
	BORIC ACID, H_3BO_3		
1	VVS	14.0	7.0
2	W	17.9	9.0
3	S	20.5	10.3
4	VS	26.3	13.1
5	VS	27.6	13.8
6	S	29.5	14.7
7	W	30.1	15.0
8	W	32.5	16.3
9	W	34.6	17.3
10	VVS	39.0	19.0
11	S	41.8	20.9
12	VW	43.6	21.8
13	VW	44.6	22.3
14	S	52.8	26.4
15	W	54.8	27.4
16	VW	57.0	28.5
17	VW	59.2	29.6
18	VW	65.1	32.5
19	VVW	69.2	34.8
20	VVW	72.5	36.3
21	W	80.2	40.2
22	VW	82.0	41.0
	METABORIC ACID, HBO_2		
1	S	12.5	6.3
2	VVS	20.5	10.2
3	W	26.7	13.4
4	VVS	28.6	14.3
5	S	32.6	16.3
6	S	34.7	17.4
7	W	36.6	18.3
8	S	40.4	20.4
9	W	42.3	21.2
10	S	44.7	22.5
11	VVW	45.8	22.9
12	VVW	48.3	24.1
13	W	48.7	24.3
14	W	50.4	25.4
15	VW	52.9	26.5
16	VW	54.9	27.5
17	VVW	60.1	30.0
18	VVW	63.2	31.6
19	VVW	65.1	32.5

S, strong. VS, very strong. W, weak. VVS, very, very strong, etc. The positions of the lines are given without checking. There may be a slight correction, owing to inaccuracy of centering of the specimen in the camera. Some of the weaker lines may be due to beta radiation.

The X-ray pictures were made with filtered copper Kα 1,2-radiation. The powders were enclosed in Pyrex glass capillary tubes of very small size and thin wall (0.5 mm. diameter, 0.03 mm. thickness). The powders were heat-treated in the tubes to expel moisture absorbed during the filling, after which the tubes were sealed by a very small flame. In this way photographs were obtained from specimens uncontaminated by moisture. Measurements of the lines are given in Table I.

The solubility curve of the crystalline oxide was sought, which can be added to the diagram of von Stackelberg, Quatram and Dressel. See Table II, also Fig. 2.

Table II

Solubility of Crystalline B_2O_3

Temp., °C.	B_2O_3 in the liquid, %
460–470	99.6
310–315	85.0
245–250	82.8
215–220	80.1

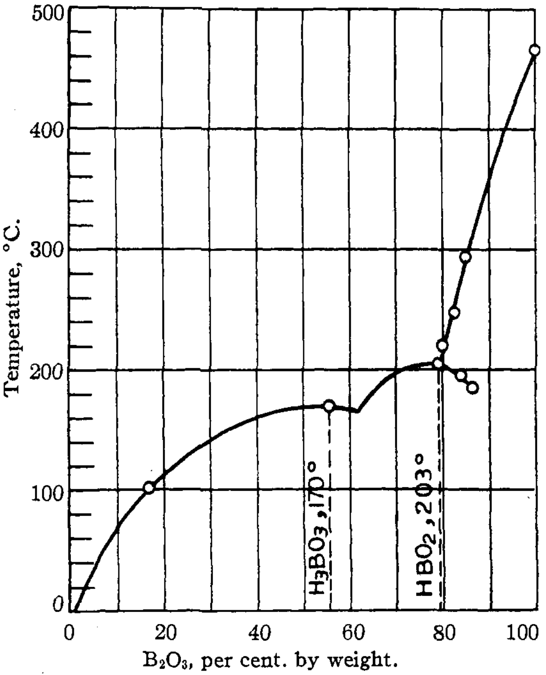

Fig. 2.—The system H_2O–B_2O_3 (after von Stackelberg, Quatram and Dressel) with addition of a solubility curve of crystalline B_2O_3.

The solubilities were determined by enclosing 25 g. of crystalline oxide with small amounts of boric acid in sealed tubes of Pyrex glass, which were kept in electric ovens at the temperatures given until it was thought that equilibrium of liquid and solid had been attained. (The time was five days at 250°, and one day at the other temperatures.) A portion of the liquid was drained from the solid by tilting the tube, it was solidified by rapid cooling, and was removed for analysis by breaking the glass tube.

The analysis was performed by hydrating the samples under water to H_3BO_3, drying the acid at 35°, weighing, and calculating the B_2O_3 content by use of the factor 0.5631. The accuracy of this method, from a check using a known weight of boric acid, is believed to be better than 99.6%.

A rod of technical grade boric oxide glass, prepared by fusion at 900–1000°, was found by the analysis to contain 98.8% B_2O_3.

This new crystalline oxide can be prepared in a nearly anhydrous form and of a high state of purity. It may find uses in the arts.

Thanks are due Dr. L. T. Bourland for the X-ray investigations.

Summary

Fused boric acid, held for days at 225–250° and retaining 8 to 15% water, was found to develop crystals, giving up its water and attaining finally the state of a stony solid. By "seeding" such a liquid, this change is induced to proceed immediately. This solid is essentially anhydrous boric oxide. The X-ray picture shows it to be crystalline. Its solubility curve is given. Its melting point is 460–470°, its density is 2.42.

East Pittsburgh, Pa. Received October 15, 1937