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STUDIES OF BORATE MINERALS (VII): *X*-RAY STUDIES OF AMMONIOBORITE, LARDERELLITE, AND THE POTASSIUM AND AMMONIUM PENTABORATE TETRAHYDRATES*

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ABSTRACT

Synthetic ammonioborite and the ammonium and potassium pentaborate tetrahydrates have been studied by *x*-ray single-crystal techniques. The results for the tetrahydrates are in agreement with those presented by Cook and Jaffe (1957). Ammonioborite is monoclinic $C2/c-C_{2h}^6$ (or less likely, $Cc-C_s^4$), with $a=25.27\pm0.05$, $b=9.65_1\pm0.03$, $c=11.56\pm0.03$ Å; $\beta=94°17.5'\pm05'$. Instead of $(NH_4)_2O\cdot 5B_2O_3\cdot 5H_2O$ (Schaller, 1933), the ammonioborite formula proposed here is $(NH_4)_2O\cdot 5B_2O_3\cdot 5\frac{1}{3}H_2O$; this gives the best agreement with present chemical and crystallographic data. Indexed *x*-ray powder data are given for the three substances named above; observed powder data are given for larderellite.

INTRODUCTION

In continuation of a systematic investigation of borate minerals the *x*-ray crystallography of synthetic ammonioborite and of the compounds, ammonium and potassium pentaborate tetrahydrate, have been examined. *X*-ray powder data for these compounds and for larderellite have also been determined.

The chemical formulas of the hydrated ammonium borate minerals, larderellite and ammonioborite, have been considered as uncertain in the mineralogical literature. Palache, Berman, and Frondel (1951) list the formula $(NH_4)_2O\cdot 5B_2O_3\cdot 5H_2O$ for both minerals, in agreement with the formula originally proposed by d'Achiardi (1930) for larderellite. In his original description of the new mineral ammonioborite, Schaller (1933) assigned the same formula to it and suggested that larderellite and ammonioborite were dimorphous. In the present study single-crystal *x*-ray measurements are combined with the experimentally observed density to derive a chemical formula for ammonioborite which can be compared with the formula obtained by the usual analytical chemical methods. Unfortunately, because larderellite does not occur in crystals large enough for either single-crystal *x*-ray work or density determination, its formula cannot be similarly derived. A preliminary account of this work was given previously (Clark and Christ, 1956).

EXPERIMENTAL TECHNIQUES

The crystals used in this study were obtained from W. T. Schaller, who supplied synthetic preparations of ammonioborite, ammonium pentaborate tetrahydrate (APT), and potassium pentaborate tetra-

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hydrate (KPT), as well as samples of natural larderellite and ammonioborite from Larderello, Italy. APT and KPT are well-known salts; a method of synthesis is given by Schaller (1933). Ammonioborite can be prepared in sizes appropriate for single-crystal study by crystallizing APT from water solution at room temperature as directed by Schaller (1933), decanting excess solution and maintaining the resulting system at 95° C. for several weeks (Schaller, private communication). Synthetic ammonioborite was used throughout the present study, the identity of the natural and synthetic materials having been established by comparison of optical and *x*-ray powder data.

Single-crystal *x*-ray studies were made with quartz-calibrated precession cameras using both Mo/Zr and Cu/Ni radiations (λ MoKα=0.7107 Å; λ CuKα=1.5418 Å). Film measurements were corrected for both horizontal and vertical film shrinkage. A 114.59 mm. diameter power camera was used with Cu/Ni radiation to obtain the powder films. Measurements on the ammonioborite powder film were corrected for film shrinkage; for all the other powder films, shrinkage corrections were found to be negligible. Interplanar spacings were calculated down to values of 1.5 Å on a Datatron computer, using a program developed by D. E. Appleman. Indices of refraction were examined as necessary to establish agreement with those previously reported; optical orientation was checked on several crystals by matching to an appropriate index oil a crystallographic direction previously identified from precession *x*-ray work. Density determinations were made both with the Berman balance and with a pycnometer.

TABLE 1. CRYSTALLOGRAPHIC DATA FOR SYNTHETIC AMMONIOBORITE

Symmetry: monoclinic			
a	25.27 ±0.05 Å	Space Group	$C2/c-C_{2h}^6$ (or less likely, $Cc-C_s^4$)
b	9.65_1±0.03	Volume	2811 Å^3
c	11.56 ±0.03	Cell Contents	$12[(NH_4B_5O_8\cdot 2\frac{2}{3}H_2O]$
β	94°17.5′±05′	Density (calc.)	1.758 g.cm.$^{-3}$
		(obs.)	1.765±0.004 (pycnometer)

X-RAY STUDY OF AMMONIOBORITE

The habit of natural ammonioborite crystals was described by Schaller (1933). The synthetic crystals have a similar habit, *i.e.*, tabular, somewhat elongated, with truncated edges. The cell constants found from single crystal *x*-ray examination are given in Table 1; ammonioborite is monoclinic, possible space groups being $Cc-C_s^4$ or $C2/c-C_{2h}^6$. Piezoelectric tests were made on the crystals with an apparatus of the Giebe-Scheibe type. The negative results, taken together with the holohedral morphology, strongly indicate the presence of a center of symmetry. The most probable space group is therefore $C2/c-C_{2h}^6$.

Description of the morphology of the synthetic crystals in terms of the *x*-ray cell is as follows: tabular on {100}, elongated parallel to [001], with forms {010}, {310}, and {311} commonly observed. Occasionally crystals are found with {010} dominant. Such crystals can be distinguished by optical examination, the optical orientation being $Y=b$, $Z\wedge c=7°$. Clark and Christ (1956) reported that optical examination showed ammonioborite to be triclinic; further optical studies prove the crystals are in fact monoclinic. Schaller (1933) describes inclined extinction as found on the "large face" and states that the obtuse bisectrix X emerges from this face. However, when inclined extinction is observed, the crystals are lying on {010} with the optic normal Y(=*b*) emerging.

X-ray powder data for ammonioborite are given in Table 2, which lists both observed and calculated interplanar spacings, the latter for $d \geq 2.600$ Å. All observed lines are satisfactorily accounted for by the chosen cell.

The observed density of ammonioborite is 1.765 ± 0.004 g.cm.$^{-3}$. For the experimentally determined cell volume of 2811 Å^3 (Table 1), a total of 6.1 formula units of $(NH_4)_2O \cdot 5B_2O_3 \cdot 5H_2O$ are found. This number is not as close to an integer as would be expected from the accuracy of the data. If 6 formula units are assumed together with the experimentally determined cell volume, a density of 1.737 g.cm.$^{-3}$ is calculated. The variation between calculated and observed densities is about 1.5%; these results indicate a re-examination of the assumed chemical formula is in order. Calculations based on the assumption that variation in water ratio alone is required give the following data:

Oxide formula	*Reduced formula*	*Calculated density*
$(NH_4)_2O \cdot 5B_2O_3 \cdot 5H_2O$	$NH_4B_5O_8 \cdot 2\frac{1}{2}H_2O$	1.737 g.cm.$^{-3}$
$(NH_4)_2O \cdot 5B_2O_3 \cdot 5\frac{1}{3}H_2O$	$NH_4B_5O_8 \cdot 2\frac{2}{3}H_2O$	1.758
$(NH_4)_2O \cdot 5B_2O_3 \cdot 5\frac{1}{2}H_2O$	$NH_4B_5O_8 \cdot 2\frac{3}{4}H_2O$	1.769

These results indicate that the last two formulas give better agreement between observed and calculated densities.

Chemical analyses made by Schaller (private communication) subsequent to his 1933 paper, but as yet unpublished, are in excellent as well as best agreement with the second oxide formula, $1:5:5\frac{1}{3}$. The monoclinic symmetry is such that positions of no less than fourfold multiplicity are indicated. For $6[(NH_4)_2O \cdot 5B_2O_3 \cdot 5\frac{1}{3}H_2O]$ per cell the total number of each type of atom is some integral multiple of four,

TABLE 2. *X*-RAY POWDER DATA FOR SYNTHETIC AMMONIOBORITE, $NH_4B_5O_8 \cdot 2\frac{2}{3}H_2O$

Monoclinic $C2/c$: $a=25.27\pm0.05$, $b=9.65_1\pm0.03$, $c=11.56\pm0.03$ Å; $\beta=94°17.5'\pm05'$

Measured*		Calculated†		Measured*		Calculated	
I	d_{hkl}	d_{hkl}	hkl	I	d_{hkl}	d_{hkl}	hkl
15	12.5	12.60	200			2.963	$\bar{2}23$
40	8.98	9.01	110			2.947	$\bar{6}03$
		7.19	$\bar{1}11$			2.926	$\bar{3}31$
<3	7.05	7.01	111			2.888	331
15	6.33	6.34	310			2.886	223
		6.30	400	60	2.876	2.882	004
		5.764	002			2.856	$\bar{2}04$
60	5.70	5.690	$\bar{3}11$			2.855	$\bar{8}02$
30	5.44	5.425	311			2.845	$\bar{6}22$
		5.396	$\bar{2}02$	10	2.822	2.826	712
3	5.10	5.099	202			2.822	513
		4.916	$\bar{1}12$			2.803	$\bar{1}32$
20	4.82	4.826	020			2.781	132
		4.798	112			2.777	$\bar{4}23$
		4.506	220	10	2.763	2.767	$\bar{1}14$
		4.467	510			2.765	204
		4.451	021			2.724	114
		4.420	$\bar{4}02$			2.713	622
15	4.37	4.389	$\bar{3}12$			2.712	530
		4.262	$\bar{5}11$			2.698	$\bar{4}04$
		4.236	$\bar{2}21$			2.694	$\bar{3}32$
	4.20	4.200	600			2.689	910
20b	to	4.160	221			2.681	$\bar{3}14$, 802
	4.15	4.149	312			2.664	$\bar{5}31$
		4.103	402			2.661	$\bar{9}11$
		4.076	511		2.671	2.653	423
		3.831	420	5 to 10, b	to	2.638	820
8	3.69	3.700	022		2.629	2.635	332
		3.686	$\bar{4}21$			2.628	$\bar{7}13$
		3.650	$\bar{5}12$			2.616	531
		3.597	$\bar{2}22$			2.607	$\bar{8}21$
10	3.58	3.587	421	3	2.578		
		3.569	$\bar{1}13$	3	2.468		
		3.522	$\bar{6}02$	<3	2.392		
4	3.49	3.505	222	3	2.365		
		3.501	113	15	2.324		
		3.423	512	5	2.262		
10	3.37	3.373	710	5	2.189		
		3.371	$\bar{3}13$	5	2.176		
		3.300	$\bar{7}11$	5	2.122		
		3.280	602	8	2.076		
3	3.26	3.259	$\bar{4}22$	5	2.032		
		3.206	313	5	1.989		
		3.191	130	5	1.963		
		3.178	711	10	1.920		
100	3.16	3.168	620	5	1.888		
		3.150	800	4	1.821		
		3.126	422	5	1.794		
100	3.09	3.100	$\bar{6}21$	<3	1.752		
		3.083	$\bar{1}31$	4	1.711		
		3.068	131	<3	1.661		
		3.014	$\bar{5}13$	<3	1.614		
50	3.01	3.012	621	5	1.581		
		3.006	023	plus additional lines			
		3.004	712, 330	all with $I\leq4$			

* Corrected for film shrinkage; b = broad. Radiation: Cu/Ni, λ CuKα = 1.5418 Å. Lower limit of 2θ measurable: approximately 7° (13 Å). Film no. 8938.

† All calculated spacings listed for $d_{hkl}\geq 2.600$ Å.

TABLE 3. X-RAY POWDER DATA FOR LARDERELLITE, $NH_4B_5O_8 \cdot 2\frac{1}{2}H_2O$

Measured* I	d_{hkl}	I	d_{hkl}	I	d_{hkl}
50	9.45	25	2.816	25	1.887
18	5.91	35	2.713	25	1.882
25	5.79	12	2.663	4	1.855
71	5.44	18	2.623	4	1.818
50	5.12	6	2.545	2	1.790
100	4.70	6	2.476	4	1.775
18	4.60	6	2.444	2	1.764
25	4.30	9	2.416	2	1.730
25	3.99	18	2.325	4	1.710
4	3.88	12	2.257	4	1.683
18	3.81	4	2.206	4	1.669
18	3.66	25	2.156	4	1.623
4	3.53	4	2.138	4	1.615
12	3.45	4	2.124	4	1.578
12	3.42	6	2.094	4	1.561
12	3.34	35	2.041	4	1.536
35	3.14	12	2.013	4	1.501
71	2.960	12	1.989	4	1.482
100	2.921	8	1.937	plus additional	
100	2.887	8	1.923	weak lines	

* Correction for film shrinkage negligible. Radiation: Cu/Ni, λ CuKα=1.5418 Å. Lower limit of 2θ measurable: approximately 7° (13 Å). Film No. 11101.

whereas for $6[(NH_4)_2O \cdot 5B_2O_3 \cdot 5H_2O]$ the total number of oxygen atoms is not an integral multiple of four. Both chemical and crystallographic evidence thus point to $(NH_4)_2O \cdot 5B_2O_3 \cdot 5\frac{1}{3}H_2O$ as the most probable formula for ammonioborite in view of the present data.

X-RAY STUDIES OF LARDERELLITE

Larderellite has not been synthesized and has been found in nature only as a finely divided crystalline powder, with crystals too minute for single-crystal x-ray study. The small quantity of available material and the size of the crystals have made determination of the density infeasible.

Monoclinic symmetry has been assigned to larderellite in the past (Palache, Berman and Frondel, 1951), and examination of the powder pattern seems to rule out all except triclinic and monoclinic symmetries. The observed interplanar spacings are shown in Table 3; the number of these spacings with relatively large d-values indicates a large cell. Assuming monoclinic symmetry, trial-and-error methods of indexing the pattern were tried, but without an observed density value as a check, the results were not considered to be conclusive. Larderellite and ammonioborite can be differentiated both by optical examination and from *x*-ray powder patterns.

X-RAY STUDIES OF APT AND KPT

Cook and Jaffe (1957) have reported on the crystallographic, elastic, and piezoelectric properties of these two borates. Our independent crystallographic studies were completed prior to publication of the Cook and Jaffe paper, and our results are in complete agreement with theirs. A comparison of their crystallographic data with ours is given in Table 4. The densities reported by Cook and Jaffe (1957) are not

TABLE 4. CRYSTALLOGRAPHIC DATA FOR AMMONIUM PENTABORATE TETRAHYDRATE AND POTASSIUM PENTABORATE TETRAHYDRATE

Space group: $Aba2-C_{2v}^{17}$

	$NH_4B_5O_8 \cdot 4H_2O$		$KB_5O_8 \cdot 4H_2O$	
	Cook and Jaffe (1957)	Present Study	Cook and Jaffe (1957)	Present Study
a	11.324±0.002 Å	11.33 ±0.02 Å	11.065±0.002 Å	11.07 ±0.02 Å
b	11.029±0.001	11.01 ±0.02	11.171±0.001	11.15 ±0.02
c	9.235±0.004	9.22_2±0.02	9.054±0.0006	9.03_8±0.02
Volume	$1153._4$ Å^3†	—	$1119._1$ Å^3†	—
Cell Contents	$4[NH_4B_5O_8 \cdot 4H_2O]$		$4[KB_5O_8 \cdot 4H_2O]$	
Density (calc.)	1.567 g.cm.$^{-3}$†	—	1.740 g.cm.$^{-3}$†	—
(obs.)	—	1.56_7±0.005	—	1.73_5±0.005

† Calculated by present authors from data of Cook and Jaffe (1957).

designated as calculated or observed; however, our observed values are in excellent agreement with the densities calculated from their cell constants.

Apparently no indexed *x*-ray powder data have been published for either APT or KPT, although observed interplanar spacings for KPT are listed on ASTM cards 3-0107, 3-0108. Table 5 presents both observed and calculated interplanar spacings for the two substances, calculated values being given for $d \geq 1.650$ Å. ASTM data for KPT have not been repeated here, although they are in agreement with those of the present study, because the present observations are in closer accord with the calculated values. In the APT pattern two lines were found having interplanar spacings that do not correspond to any calculated for this material, and all efforts to identify the lines as belonging to another substance failed. Possibly some alteration product is formed during preparation of the sample for the powder pattern.

TABLE 5. *X*-RAY POWDER DATA FOR AMMONIUM PENTABORATE TETRAHYDRATE, $NH_4B_5O_8 \cdot 4H_2O$, AND POTASSIUM PENTABORATE TETRAHYDRATE, $KB_5O_8 \cdot 4H_2O$

Orthorhombic *Aba*2:

$NH_4B_5O_8 \cdot 4H_2O$: $a = 11.324 \pm 0.002$, $b = 11.029 \pm 0.001$, $c = 9.235 \pm 0.004$ Å
$KB_5O_8 \cdot 4H_2O$: $a = 11.065 \pm 0.002$, $b = 11.171 \pm 0.001$, $c = 9.054 \pm 0.0006$ Å
(Values of the cell constants from Cook and Jaffe, 1957)

$NH_4B_5O_8 \cdot 4H_2O$				$KB_5O_8 \cdot 4H_2O$			
Measured*		Calculated†		Measured*		Calculated†	
I	d_{hkl}	d_{hkl}	*hkl*	I	d_{hkl}	d_{hkl}	*hkl*
100	6.01	6.004	111	15	5.93	5.936	111
		5.662	200	71	5.60	5.585	020
35	5.54	5.515	020			5.532	200
2	4.97	4.958	120	2	4.99	4.986	120
9	4.63	4.618	002	6	4.52	4.527	002
3	4.46	4.422	211	2	4.34	4.348	211
		3.950	220	5	3.93	3.931	220
		3.578	202	84	3.52	{3.517	022
71	3.54	3.540	022			3.503	202
9	3.46††						
85	3.38	3.379	122	100	3.36	3.352	122
18d	3.33	3.331	311	18	3.28	3.288	131
18	3.26	3.270	131			3.266	311
2	3.13	3.115	320	1	3.07	3.078	320
4	3.01	3.002	222	6	2.969	2.968	222
9	2.923	2.925	231	6	2.926	2.924	231
		2.868	113	4	2.818	2.817	113
71	2.837	2.831	400			2.793	040
		2.757	040	50	2.767	2.766	400
2	2.682	2.679	140	1	2.710	2.708	140
4d	2.631	{2.629	411	4	2.574	{2.578	213
		2.627	213			2.574	411
		2.582	322			2.545	322
12	2.532	2.533	331	12	2.517	2.517	331
		2.518	420			2.493	240
		2.479	240	2d	2.483	2.479	420
2	2.414	2.413	402	9	2.375	2.377	042
3	2.369	2.367	042			2.360	402
		2.332	313	4	2.324	2.324	142
12	2.316	{2.317	142	9	2.290	{2.294	133
		2.311	133			2.286	313

* Not corrected for film shrinkage; d = diffuse. Radiation: Cu/Ni, λ CuKα = 1.5418 Å. Lower limit of 2θ measurable: approximately 7° (13 Å). Film nos. 11151 and 11262.

† All calculated spacings listed for $d_{hkl} \geq 1.650$ Å.

†† Not indexable as APT, nor as any tested impurity.

TABLE 5 (*Continued*)

$NH_4B_5O_8\cdot 4H_2O$				$KB_5O_8\cdot 4H_2O$			
Measured*		Calculated†		Measured*		Calculated†	
I	d_{hkl}	d_{hkl}	hkl	I	d_{hkl}	d_{hkl}	hkl
		2.309	004	4	2.259	2.263	004
		2.226	340			2.226	340
6	2.211	2.211	422	21	2.181	2.184	242
		2.184	242			2.174	422
18	2.181	2.180	431	4	2.158	2.159	233
		2.179	233			2.157	431
		2.157	511	2	2.129	2.129	151
		2.138	204	6	2.115	2.111	511
		2.130	024			2.098	024
9	2.102	2.108	151	2	2.093	2.095	204
		2.095	520	3	2.062	2.061	124
		2.093	124			2.057	502
2	2.050	2.048	413	1	2.021	2.019	251
15	2.005	2.006	251, 342			2.006	413
		2.001	333	4	1.999	1.998	342
		1.993	224	2	1.979	1.979	333
		1.975	440			1.965	440
< 6**	1.934††						
	1·907	1.908	522	3	1.962	1.961	224
		1.888	531	4	1.872	1.873	522
		1.887	600			1.870	351
		1.865	351			1.862	060, 531
	1.859	1.855	324			1.844	600
		1.838	060			1.836	160
d	1.820	1.824	611	2	1.825	1.823	324
		1.816	442	4	1.802	1.803	442
		1.814	160			1.789	433
		1.813	433			1.784	611
		1.800	513			1.772	153
		1.799	115			1.765	260, 115
		1.789	404	3d	1.761	1.762	513
		1.786	620			1.758	044
	1.770	1.771	153			1.752	404
		1.770	044			1.751	620
		1.750	540	2	1.738	1.737	144
	1.748	1.749	144			1.734	540
		1.748	260			1.722	062
		1.747	602	2	1.708	1.708	602, 253
		1.734	215			1.707	451
		1.710	451			1.701	162, 215
		1.709	253	1	1.675	1.676	244

(*Continued on next page*)

** I<6 for this line and succeeding lines.

TABLE 5 (*Continued*)

$NH_4B_5O_8 \cdot 4H_2O$				$KB_5O_8 \cdot 4H_2O$			
Measured*		Calculated†		Measured*		Calculated†	
I	d_{hkl}	d_{hkl}	*hkl*	I	d_{hkl}	d_{hkl}	*hkl*
	1.706	1.708	062			1.671	424
		1.702	424			1.662	360
		1.690	244	4d	1.611		
		1.689	162	2	1.558		
		1.665	622	6	1.543		
		1.653	360	plus additional lines, I≤6			
		1.652	631				
	1.636						
	1.539						
	1.435						
plus additional weak lines							

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