

CRYSTAL GEOMETRY OF SOME ALKALI SILICATES

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ABSTRACT

α - $\text{Na}_2\text{Si}_2\text{O}_5$ (the high-temperature form) is orthorhombic $Pnam$, pseudo- $Pnab$. $a = 15.45 \pm 0.03$, $b = 4.909 \pm 0.005$, $c = 6.428 \pm 0.015$ Å. $Z = 4$. Density (g/cm^3) = 2.47 ± 0.03 (obs.), 2.48 (calc.). Thick tabular {100}. Cleavage {100}.

β - $\text{Na}_2\text{Si}_2\text{O}_5$ is monoclinic $P2_1/a$. $a = 12.307 \pm 0.005$, $b = 4.849 \pm 0.003$, $c = 8.124 \pm 0.004$ Å, $\beta = 104.12 \pm 0.005^\circ$. $Z = 4$. Density (g/cm^3) = 2.57 ± 0.10 (obs.), 2.542 (calc.). Thin tabular {100}, elongated [010]. Cleavages {100} and {001}. Dual twinning, twin plane and composition plane (100).

$\text{Li}_2\text{Si}_2\text{O}_5$ is orthorhombic, diffraction aspect Ccc^* . $a = 5.80 \pm 0.02$, $b = 14.66 \pm 0.05$, $c = 4.806 \pm 0.015$ Å. $Z = 4$. Density (g/cm^3) = 2.454 (lit., at 25°C .), 2.438 (calc.).

Li_2SiO_3 is orthorhombic, diffraction aspect Cc^{**} , probable space group $Ccm2$. $a = 5.43 \pm 0.02$, $b = 9.41 \pm 0.03$, $c = 4.660 \pm 0.015$ Å. $Z = 4$. Density (g/cm^3) = 2.520 (lit., at 25°C .), 2.50 (calc.).

INTRODUCTION

In the course of a survey of soluble silicates, we examined crystals of two polymorphic forms of sodium disilicate $\text{Na}_2\text{Si}_2\text{O}_5$, lithium disilicate $\text{Li}_2\text{Si}_2\text{O}_5$, and lithium metasilicate Li_2SiO_3 . All x -ray photographs were taken with $\text{CuK}\alpha$ radiation ($\lambda = 1.5418$ Å). The sodium compounds were prepared by Dr. G. W. Morey, the lithium compounds by Dr. F. C. Kracek.

SODIUM DISILICATES

The phase diagram $\text{Na}_2\text{O}-\text{Si}_2\text{O}$ has been described by Morey and Bowen (1924) and by Kracek (1930). The melting point of $\text{Na}_2\text{Si}_2\text{O}_5$ is $874 \pm 1^\circ$. Kracek has obtained three polymorphic forms, distinguished by their powder patterns, on which he reports as follows (private communication). The lowest-temperature form is obtained only on crystallization from the glass between 500 and 580° . It has not yielded any single crystals and its powder pattern has not been indexed. It appears to be a metastable modification. Hydrothermally, between 480 and 670° , another form (β) crystallizes. This β form is also obtained from the glass between 580 and 670° . Above 670° the high-temperature form (α) appears. Both α and β forms are somewhat hygroscopic. The transition from β to α is sluggish; at 695° it takes several days. Attempts to transform the α to the β -form have been unsuccessful. Further details on

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occurrence and properties will be published in a forthcoming paper from the Geophysical Laboratory.

(1) α - $\text{Na}_2\text{Si}_2\text{O}_5$

α -Sodium disilicate is orthorhombic, apparently holohedral. Single crystals measuring 3 to 4 mm. in maximum dimension have been found. They form milky white plates, thick to very thick tabular on $\{100\}$, slightly elongated $[010]$. They possess one very good and easy cleavage $\{100\}$, which gives mediocre reflections. All other reflections are very poor. The plate is beveled by a rhombic prism, which is symbolized $\{201\}$ in order to conform with the x -ray results (see below). A small $\{010\}$ face is present, but the pinacoid $\{001\}$ is missing. The measured angle $(100):(201) = 49\frac{3}{4}^\circ$ yields the crude axial ratio $c/a = \frac{1}{2} \tan 40\frac{1}{4}^\circ = 0.42$, which agrees with $c/a = 0.416$ obtained by x -rays.

A sample of fibrous sodium disilicate (not commercially available) was given to us by the Philadelphia Quartz Company. It proved to be the α -form.

The optical data given by Bowen (in Kracek, 1930a) are as follows: $n_\alpha = 1.497$, $n_\gamma = 1.508$, biaxial negative, $2V = 50-55^\circ$, two cleavages parallel to $\beta\gamma$ and $\gamma\alpha$.

Weissenberg photographs were taken about the three axes. The x -ray extinctions indicate the diffraction aspect Pna^* , which is compatible with two space groups: $Pna2$ and $Pnam$. Inasmuch as the goniometric measurements seem to show that both the a and the b axes are 2-fold axes, the crystal is most likely holohedral with space group $Pnam$. In addition to the systematic space-group extinctions, near-extinctions are also observed—the $hk0$ reflections with k odd are very weak.¹ They indicate a pseudo b glide plane parallel to (001) and a pseudo space group $Pnab$.

The cell dimensions were refined with the help of a powder pattern (taken by Dr. H. Yoder on the Philips back-reflection x -ray spectrometer). They are: $a = 15.45 \pm 0.03$, $b = 4.909 \pm 0.005$, $c = 6.428 \pm 0.015$ Å. This choice of axes is made to bring out the relationship with the monoclinic form, so that the cleavage is symbolized $\{100\}$ and the b unit length is nearly the same in both forms. The density, based on three determinations on the Berman balance, with crystals weighing 4 to 5 mg, is 2.47 ± 0.03 g/cm³. With 4 formula units per cell, the calculated density is 2.48 g/cm³.

Fiber diagrams obtained with the material from the Philadelphia

¹ Only 210, 13.1.0, and 17.1.0 are observed at all. They were obtained on two different photographs, taken with different samples (b -axis first layer), and are therefore considered reliable reflections.

Quartz Company show that the b axis is the fiber axis. The reflections are drawn out along arcs which subtend an angle of 13° at the center of the film. It follows that the fibrils are not perfectly parallel to the fiber axis but may deviate from it as much as $6\frac{1}{2}^\circ$. The diffracted arcs are sharp, indicating a fibril thickness of at least 1000 Å. The fibrous material is as hygroscopic as the single crystals.

(2) β - $\text{Na}_2\text{Si}_2\text{O}_5$

β -Sodium disilicate is monoclinic, apparently holohedral. Some single crystals measure up to 2 mm. in maximum dimension, most of them less than one mm. They form colorless pseudo-hexagonal plates or laths, thin tabular on $\{100\}$ and elongated $[010]$. They show two cleavages: $\{100\}$, eminent, nearly micaceous, and very easy; $\{001\}$, good and fairly easy, indicated by $[010]$ striations on $\{100\}$.

Except for the faces of the pinacoid $\{100\}$, which give excellent reflections, the crystals are of poor quality for optical goniometry. Three relatively satisfactory angles, namely, $(100):(001) = 75^\circ 45'$, $(100):(201) = 31^\circ 25'$, $(011):(01\bar{1}) = 63^\circ 20'$, were obtained on a two-circle instrument. They yield the following crude axial elements:

$$a:b:c = 2.49_3:1:1.67_1; \quad \beta = 104^\circ 15'$$

The forms observed are: $\{100\}$ dominant; $\{001\}$, $\{011\}$, $\{201\}$, and $\{20\bar{1}\}$, common; $\{101\}$, $\{401\}$, $\{601\}$, uncertain. The occurrence of $\{001\}$ as a subordinate form, with $\{200\}$ as the habit-controlling form, is anomalous. The morphological development is otherwise consistent the space group $P2_1/a$ determined by x -rays (see below). The latter requires the point group to be $2/m$, thus confirming the holohedry.

Dual twinning is universal, with twin plane (100) . It is twinning by reticular pseudo-merohedry, due to the quasi-perpendicularity of $[310]$ and (100) . The twin index is 3, its obliquity $1^\circ 21'$. The composition surface is planar and parallel to the twin plane, as required by theory. Owing to the extreme thinness of the plates, such a contact twin simulates crystals in parallel orientation. The two individuals, lying on (100) , extinguish of course simultaneously between crossed nicols, so that this kind of twinning may easily pass unnoticed, even optically.

The refractive indices were re-measured by Dr. Jewel Glass: $n_\gamma = 1.515$ lies along $[010]$; the second index (1.510) measured in the (100) plane and the index (1.500) measured perpendicular to it, do not differ much from the principal indices n_β and n_α respectively, as the interference figure obtained in convergent light shows the acute bisectrix nearly perpendicular to (100) . The optical character is negative ($2E = 105^\circ$, in Morey, 1914).

Weissenberg photographs were taken about $[100]$ and $[010]$. The space

TABLE 1

β -Na₂Si₂O₅
 $a = 12.307 \pm 0.005$ $b = 4.849 \pm 0.003$ $c = 8.124 \pm 0.004 \text{ \AA}$
 $\beta = 104.12 \pm 0.005^\circ$

Qual.*	2 θ obs. Cu K α	d obs.	Q obs.	Q calc.	2 θ calc. Cu K α	hkl
1 R	11.24	7.871	.01614	.01611	11.23	001
9 R	14.84	5.970	.02806	.02808	14.84	200
3 R	16.27	5.448	.03369	.03381	16.30	20 $\bar{1}$
				.04955	19.76	110
9 R	20.74	4.283	.05452	.05457	20.75	201
4 R	21.53	4.127	.05871	.05864	21.52	011
				.06047	21.86	11 $\bar{1}$
10 R	22.57	3.939	.06444	.06444	22.57	002
3	23.65	3.762	.07066	.07061	23.64	210
				.07085	23.68	111
				.07177	23.84	20 $\bar{2}$
8 R	24.58	3.622	.07624	.07634	24.59	21 $\bar{1}$
				.09710	27.80	211
1 R	28.71	3.109	.10344	.10361	28.73	11 $\bar{2}$
				.10571	29.03	310
				.10625	29.11	31 $\bar{1}$
				.10697	29.21	012
9 R	29.28	3.050	.10749	.10768	29.30	40 $\bar{1}$
5 R	29.95	2.983	.11235	.11232	29.95	400
8 R	30.07	2.972	.11324	.11327	30.07	202
				.11430	30.21	21 $\bar{2}$
				.12437	31.55	112
				.13526	32.94	40 $\bar{2}$
				.13739	33.21	311
2 R	33.38	2.684	.13879	.13903	33.41	31 $\bar{2}$
6 R	33.76	2.655	.14188	.14195	33.77	20 $\bar{3}$
2 R	34.15	2.625	.14508	.14499	34.14	003
5 R	34.66	2.588	.14931	.14918	34.65	401
				.15021	34.77	41 $\bar{1}$
				.15485	35.29	410
2 R	35.42	2.532	.15597	.15580	35.40	212
5 R	37.07	2.423	.17032	.17012	37.05	020
				.17714	37.83	120
				.17779	37.90	41 $\bar{2}$
1 R	38.21	2.353	.18056	.17897	38.03	11 $\bar{3}$

TABLE 1—(continued)

Qual.	2θ obs. Cu K_{α}	d obs.	Q obs.	Q calc.	2θ calc. Cu K_{α}	hkl
2 R	38.65	2.327	.18459	.18448	38.64	$21\bar{3}$
				.18623	38.83	021
				.18752	38.97	013
				.18806	39.03	$12\bar{1}$
1 R	39.45	2.282	.19200	.19171	39.42	411
				3 R	39.76	2.265
.19820	40.11	220				
.19844	40.13	121				
.20127	40.43	$31\bar{2}$				
.20393	40.71	$22\bar{1}$				
1	40.78	2.211	.20406	.20401	40.72	$31\bar{3}$
				.20419	40.74	203
				.20821	41.15	$51\bar{1}$
1 R	41.42	2.178	.21079	.21011	41.35	113
				.21803	42.16	510
5	42.20	2.140	.21844	.21826	42.18	402
3	43.38	2.084	.23023	.22469	42.83	221
				.23059	43.41	$51\bar{2}$
				.23120	43.48	$11\bar{2}$
				.23330	43.68	320
				.23384	43.74	$32\bar{1}$
2	44.10	2.052	.23755	.23456	43.81	022
				.23759	44.10	$41\bar{3}$
				.23770	44.11	$60\bar{1}$
				.24189	44.52	$22\bar{2}$
				.24434	44.76	$20\bar{4}$
1 R	45.55	1.990	.25259	.24672	44.99	213
				.25196	45.49	122
				.25272	45.56	600
Fifteen reflections calculated						
9	49.90	1.826	.29992	.29744	49.68	$61\bar{2}$
				.29995	49.90	601
				.30029	49.93	014
				.30122	50.02	$31\bar{4}$
				.30434	50.29	$60\bar{3}$

* Qual. refers to the quality (not the height) of the peak; it estimates, on a scale of 1 to 10, the accuracy with which the peak can be located. *R* stands for "resolved" and indicates that only one reflection can account for the peak.— $Q=1/d^2$ (*Q* stands for "quadratic"). *Q* calc. and 2θ calc. are computed from the unit-cell dimensions given at the head of the table.

group, uniquely determined by x -rays, is $P2_1/a$. The cell dimensions, refined by means of a powder pattern also taken by H. Yoder (Table 1), are: $a = 12.307 \pm 0.005$, $b = 4.849 \pm 0.003$, $c = 8.124 \pm 0.004$ Å and $\beta = 104.12 \pm 0.005^\circ$. With 4 formula units per cell, the calculated density is 2.542 g/cm³. The observed density is 2.57 ± 0.10 g/cm³, the high uncertainty being due to the small size of the crystal—0.4 mg.

Our powder data differ sufficiently from those given in the literature (Burkhart and Imhoff, 1947) to warrant careful comparison. Table 2 shows the results of this analysis and explains the discrepancies.

LITHIUM DISILICATE

As reported to us by Kracek $\text{Li}_2\text{Si}_2\text{O}_5$ was crystallized from a melt and annealed at 975° C. It melts incongruently at about 1033° C. to a more siliceous liquid and crystals of $\text{Li}_2\text{Si}_2\text{O}_3$. A rapid high-low transformation takes place at $936 \pm 3^\circ$; the high-temperature form cannot be quenched. We are therefore dealing with crystals of the low-temperature form.

Many of the "crystals" examined turned out to be glass. The true crystals are small {010} plates, slightly elongated along [001], less than 0.1 mm. long, with striations parallel to [001] and [100]. Merwin (in Kracek, 1930b) writes: "*Lithium disilicate* $\text{Li}_2\text{Si}_2\text{O}_5$ appears to be orthorhombic with three cleavages at right angles. One cleavage is micaceous, the other two are nearly perfect. The plane of the optic axes is parallel to the micaceous cleavage, and γ parallel to the intersection of the two best cleavages. Optical character is positive, $2V = 50^\circ$ to 60° . Refractive indices: $\alpha = 1.547$, $\beta = 1.550$, $\gamma = 1.558$, all probably within ± 0.001 ."

Weissenberg and precession photographs yield the diffraction aspect Ccc^* , compatible with space groups $Ccc2$ and $Cccm$. The cell dimensions are: $a = 5.80 \pm 0.02$, $b = 14.66 \pm 0.05$, $c = 4.806 \pm 0.015$ Å. With 4 formula units per cell, the calculated density is 2.438 g/cm³, as compared with an observed density of 2.454 g/cm³ at 25° C. (Jaeger and van Klooster, 1914).

LITHIUM METASILICATE

Only one form of Li_2SiO_3 exists, with melting point $1201 \pm 1^\circ$ C. (Kracek, 1930b). The compound was correctly described as orthorhombic pseudo-hexagonal by Hautefeuille and Margottet (1881), yet the Barker Index (1952) still lists it as hexagonal.

Li_2SiO_3 was melted, crystallized, and annealed at 1115° (Kracek). Most of the crystals are lath-shaped, less than 1 mm. in length, tabular on {010} and elongated along [001]; their faces give poor reflections. A few crystals, however, short-prismatic in habit, could be measured on the goniometer and proved to be pseudo-hexagonal prisms.

TABLE 2. ANALYSIS OF POWDER DATA IN LITERATURE
IN THE LIGHT OF PRESENT RESULTS

<i>hkl</i>	$d_{Lit.}^*$	$I_{Lit.}^*$	d calc.	Peak hght. obs.	Remarks
—	6.61	vw	—	—	FeK β , $d(200) = 6.00$
200	5.98	ms(4)	5.967	77	Misprint (not 3.98)
20 $\bar{1}$	5.46	vw	5.439	6	
—	4.72	vw	—	—	FeK β , $d(201) = 4.28$
110	4.57	vw	4.492	—	
201	4.26	m	4.281	25	
011	4.13	w	4.129	7	
002	3.94	m	3.940	42	
210	3.76	w	3.764	6	
111			3.757		
21 $\bar{1}$	3.63	ms(6)	3.619	18	
—	3.52	vw	—	—	Unaccounted for.
—	3.36	w	—	—	FeK β , $d(11\bar{2}, 40\bar{1}) = 3.06$
11 $\bar{2}$	3.07	m(5)	3.107	3	
310			3.076	—	
31 $\bar{1}$			3.068	—	
012			3.058	—	
40 $\bar{1}$			3.047	41	
400			2.984	47	
202	2.96	s(2)	2.971	58	
112			2.836	—	
31 $\bar{2}$	2.67	m(7)	2.682	5	
20 $\bar{3}$			2.654	23	
401			2.589	21	
41 $\bar{1}$	2.58	m(8)	2.580	—	
212			2.533	5	
020	2.42	m(9)	2.425	10	
11 $\bar{3}$	2.35	vw	2.364	3	
21 $\bar{3}$			2.328	3	
411	2.27	w	2.284	3	
40 $\bar{3}$			2.264	6	
51 $\bar{1}$			2.192	—	
113	2.19	vw	2.182	2	
510			2.141	—	
402	2.14	m(10)	2.140	13	
51 $\bar{2}$			2.082	4	
41 $\bar{3}$	2.05	w	2.052	4	
600	1.99	w	1.989	2	
Sixteen reflections calculated, four of them observed by B. and I.					
601	1.82	s(1)	1.826	28	
etc. . . .					

* $d_{Lit.}$ and $I_{Lit.}$ refer to interplanar distances and intensities given by Burkardt and Imhoff (1947), who used unfiltered iron radiation. $d_{calc.}$ is computed from $Q_{calc.}$ of Table 1. "Peak height observed" refers to height above background on the chart, expressed on an arbitrary scale.

Weissenberg and precession photographs show that the crystal system is orthorhombic with diffraction aspect Cc^{**} , which permits the space groups $Ccmm$, $Cc2m$ or $Ccm2$. The cell dimensions are $a=5.43\pm 0.02$, $b=9.41\pm 0.03$, $c=4.660\pm 0.015$ Å. It follows that $a/b=0.577\pm 0.004$ is equal to $\tan 30^\circ=0.5774$ and that the lattice, from a purely metric point of view, is hexagonal, within the experimental accuracy. With 4 formula units per cell, the calculated density is 2.50 g/cm³, in agreement with the observed density of 2.520 g/cm³ at 25° C. (Jaeger and van Klooster, 1914).

The lath-shaped irregular crystals show parallel extinction and positive elongation (on the sign of the elongation, we confirm Jaeger and van Klooster, 1914, and disagree with Merwin, in Kracek, 1930*b*). In convergent light a flash figure² is obtained, which yields the following optical orientation: $\gamma=c$, $\alpha=a$, $\beta=b$. The crystals are biaxial positive, with medium birefringence. Judging from the pseudo-uniaxial character (Merwin, *op. cit.*), $2V$ must be small. The refractive indices on record are as follows: $n_\gamma=1.609\pm 0.004$, $n_\alpha=1.584\pm 0.002$, $B=0.025$ (Jaeger & van Klooster, 1914); $n_\epsilon=n_\gamma=1.611\pm 0.001$, $n_\omega=n_\alpha$ or $n_\beta=1.591\pm 0.001$ (Merwin, *op. cit.*)

The crystal structure of Na_2SiO_3 , the corresponding sodium salt, has recently been described by Grund and Pizy (1952), who kindly let us see their manuscript prior to publication. It consists of single chains of SiO_4 tetrahedra, parallel to the c axis and held together by sodium ions. The structure differs from that of the pyroxenes in that it has four alkali ions per Si_2O_6 link of the chain rather than two alkaline earth ions. Grund and Pizy remark that each sodium ion is coordinated to only five oxygens at distances ranging from 2.27 to 2.45 Å. Note, however, that one of these oxygens is a "dummy," as it is shared between two silicons and is therefore electrostatically neutralized. The coordination number is actually four, amazingly low for sodium. With four sodium-oxygen bonds of strength $\frac{1}{4}$, the Pauling rule is perfectly satisfied since each unshared oxygen receives four such bonds. The coordination polyhedron of sodium roughly approximates a tetrahedron.

Since the lithium ion is smaller than the sodium ion, Li_2SiO_3 and Na_2SiO_3 may be expected to have isotypic structures. Indeed the space group reported for the sodium compound is (in our orientation, with $a < b$) $Ccm2$. Its cell dimensions, $a=6.02$, $b=10.43$, $c=4.81$, are larger than those of the lithium silicate, a and b by 10.9% and 10.8% respectively, c by only 3.2% . The ratio $a/b=0.5772$ is also that required by a

² The isogyres flash out in less than 16° rotation. The possibility of an obtuse bisectrix figure is not absolutely ruled out; in this alternate interpretation, $\alpha=b$, $\beta=a$.

hexagonal lattice. The increases in the a and b lengths as one goes from Li to Na are in keeping with the increase in ionic diameter; the c length changes less as it is mostly governed by the SiO_3 chains. The structural hypothesis of chains stretching along the c axis is also supported by the optical character of Li_2SiO_3 , biaxial positive with small $2V$ and acute bisectrix parallel to c .

In the system Na_2SiO_3 - Li_2SiO_3 Kracek (1939) finds an intermediate compound NaLiSiO_3 , complete solid solution between it and Na_2SiO_3 , and limited solid solution between it and Li_2SiO_3 . The crystal structures of Li_2SiO_3 and NaLiSiO_3 have not as yet been determined.

REFERENCES

- BURKARDT, L. A., AND IMHOFF, C. E. (1947), X-ray diffraction studies of steam turbine deposits: *Ind. Eng. Chem.*, **39**, 1427-1432.
- GRUND, A., AND PIZY, M. (1952), Structure cristalline du metasilicate de sodium anhydre (abstract): *Bull. Soc. fr. Min. et Crist.*, **75**, page xxxiii (to be published *in extenso* in same journal).
- HAUTEFEUILLE, P., AND MARGOTTET, J. (1881), Sur la silice et les silicates de lithine: *Compt. Rend. Acad. Sc. Paris*, **93**, 686-691.
- JAEGER, F. M., AND VAN KLOOSTER, H. S. (1914), Studies in the field of silicate-chemistry: *Proc. Amst. Acad. Sci.*, **16**, 857-880.
- KRACEK, F. C. (1930*a*), The system sodium oxide-silica: *J. Phys. Chem.*, **34**, 1583-1598.
- KRACEK, F. C. (1930*b*), The binary system Li_2O - SiO_2 : *J. Phys. Chem.*, **34**, 2641-2650.
- KRACEK, F. C. (1939), Phase equilibrium relations in the system Na_2SiO_3 - Li_2SiO_3 - SiO_2 : *J. Am. Chem. Soc.*, **61**, 2863-2877.
- MOREY, G. W., AND BOWEN, N. L. (1924), The binary system sodium metasilicate-silica: *J. Phys. Chem.*, **20**, 1167-1179.

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