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Crystal structure of a synthetic lithium zeolite

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Auszug

Der Zeolith Li-A(BW) hat nach Barrer und White, die als erste 1951 über ihn berichteten, die Formel $LiAlSiO_4 \cdot 2H_2O$. Eine neue Untersuchung am Originalmaterial führte zur Bestimmung der rhombischen Zelle mit $a = 10{,}31$, $b = 8{,}18$, $c = 5{,}00$ Å und zu einem Strukturvorschlag in der Raumgruppe $Pna2_1$. Auf Grund von 78 beobachteten Interferenzen wurde die Struktur bis zu $R = 0{,}13$ verfeinert. Das Aluminiumsilikatgerüst besteht aus 4-, 6- und 8-gliedrigen Ringen, von denen die 4-gliedrigen zu Bändern längs der faserigen Kristalle verbunden sind, während die 8-gliedrigen Ringe Kanäle von 3,2 Å Durchmesser in der gleichen Richtung offen lassen. In jeden Kanal ist eine Säule von Wassermolekülen zentral eingelagert im Anschluß an Li-Kationen, welche sich beiderseits von 6-gliedrigen Ringen befinden.

Es werden Versuche zur Bestimmung der Raumgruppe und des Verhältnisses Al/(Si + Al) sowie ein Programm zur Verfeinerung der Atomabstände in bezug auf die vorgegebenen Werte beschrieben. Hinweise auf (Al,Si)-Ordnung wurden gefunden. Li-A(BW) weist große Ähnlichkeit mit Bikitait und Cancrinit auf.

Abstract

The zeolite Li-A(BW) was first reported by Barrer and White (1951) and given the approximate formula, $LiAlSiO_4 \cdot 2H_2O$. A recent examination of their specimens has resulted in the determination of the orthorhombic unit cell with $a = 10.31, b = 8.18, c = 5.00$ Å, and the proposal of a structure based on $Pna2_1$. The x-ray analysis was based on 78 intensity data from powder, and refined to $R = 0.13$. The aluminosilicate framework consists of 4-, 6- and 8-membered rings, the 4-membered rings linking to form ribbons running lengthwise along the fibrous crystals, while the 8-membered rings enclose channels of about 3.2 Å free diameter running likewise. A column of water molecules is situated centrally in the channel adjacent to Li cations which are located each side of the 6-membered rings. Use is described in determining the space group and the ratio Al/(Si + Al), of a program which refines distances to prescribed values. Evidence of ordering of Si and Al atoms is also found. Li-A(BW) shows much similarity to bikitaite and cancrinite.

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Introduction

Barrer and **White** (1951) described the hydrothermal synthesis of a new Li aluminosilicate which they called Li-A. In this note it is referred to as Li-A(BW). It occurred most readily in the range 150 to 250 °C and they gave its analysis as $Li_{0.87}Al_{0.97}Si_{1.05}O_4 \cdot 2H_2O$. Subsequently there have been frequent reports of its occurrence (**Aeillo** *et al.*, 1971) chiefly as an intermediate phase.

Experimental

Li-A(BW) always appears in rod-like habit (Fig. 1), but although there have been frequent reports of its occurrence, it has never been grown to sufficient dimensions for x-ray single-crystal work. The particles are however of a suitable size for electron diffraction (Fig. 2), and information drawn from this source has enabled the x-ray powder pattern (Table 1) to be indexed upon an orthorhombic cell with $a = 10.31 \pm 0.02$, $b = 8.18 \pm 0.02$ and $c = 5.00 \pm 0.01$ Å. From the noted series of extinctions the number of space groups was reduced to

Table 1. *The x-ray powder pattern of Li-A(BW)*

hkl	Int.	d_{obs}	d_{calc}	*hkl*	Int.	d_{obs}	d_{calc}
110	100	6.439 Å	6.408 Å	040	5	2.0444 Å	2.0450 Å
200	17	5.169	5.155	421	2	1.9987	1.9988
210	19	4.360	4.361	510			1.9995
011	34	4.272	4.266	312	6	1.9613	1.9626
020	5	4.093	4.090	331			1.9643
211	3	3.288	3.287	240	1	1.8994	1.9009
310	90	3.167	3.168	430	2	1.8729	1.8731
121	67	3.025	3.026	520	<1	1.8387	1.8412
221	3	2.697	2.698	322	2	1.8100	1.8124
130	6	2.635	2.636	132			1.8140
320			2.631	412	10	1.7518	1.7529
002	19	2.501	2.500	431			1.7540
410	3	2.459	2.458	340			1.7574
031	6	2.393	2.394	600	7	1.7157	1.7183
112	12	2.330	2.329	341	<1	1.6537	1.6580
321			2.328	422	<1	1.6400	1.6433
131			2.332	530			1.6447
202	2	2.247	2.249	013	2	1.6306	1.6331
411	1	2.205	2.206	440	<1	1.6000	1.6020
420	2	2.181	2.181	042	3	1.5811	1.5829
231	5	2.170	2.171	620			1.5842
212			2.169	203			1.5858
122	<1	2.090	2.089				

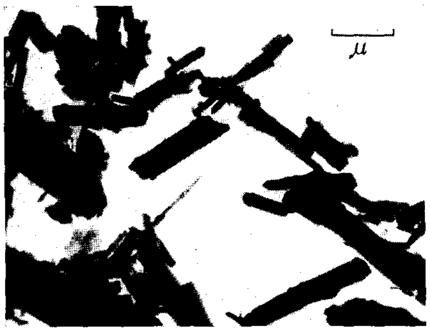

Fig. 1. Electron-micrograph of Li-A(BW) taken on a Philips EM 100

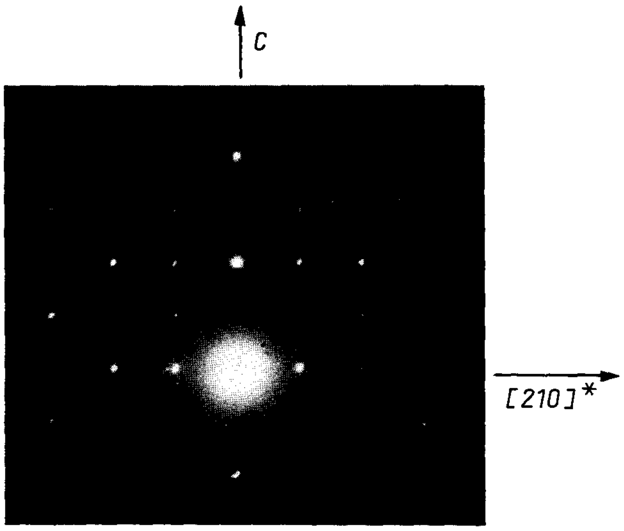

Fig. 2. Electron-diffraction pattern from a single lath

the two possibilities *Pnma* or *Pna*2_1. It was not possible to use a statistical test on the presence of a centre of symmetry, so distinguishing the two groups, owing to the few data—78 observed intensities, many of them due to overlying reflections.

Suggested framework for Li-A(BW)

The dimensions of the unit cell make a number of comparisons possible with those of other zeolites of known structure (Meier, 1968). Thus (*i*) the 5 Å corresponds to a similar dimension in cancrinite and

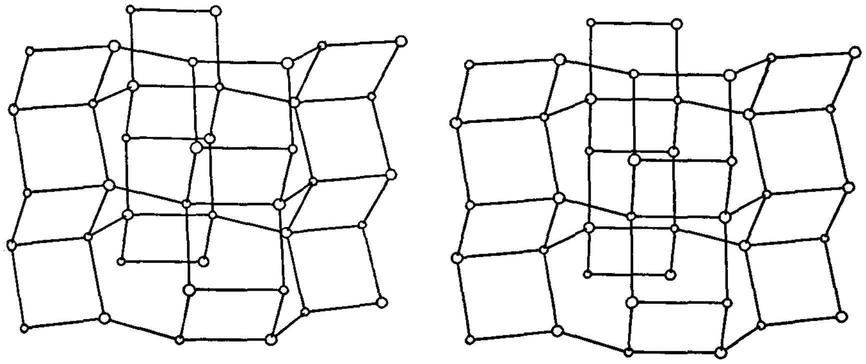

Fig. 3. Framework of Li-A(BW) drawn by ORTEP. Large spheres are Al, small spheres Si, oxygen atoms are not shown but fall roughly at the mid points of bonds. *a* axis to right; *b*, away from observer; *c*, vertical

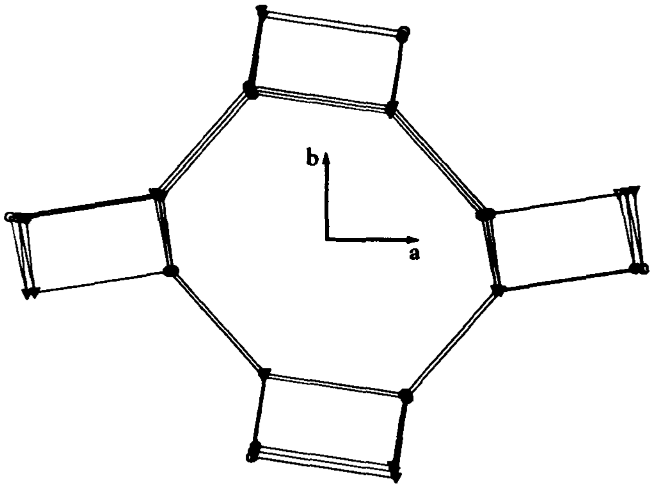

Fig. 4. Framework of Li-A(BW), looking down *c* axis showing main channel

bikitaite and undoubtedly represents a two-membered chain, (*ii*) the 8.2 Å axis compares with a similar one in tridymite where there is a folded four-membered chain and (*iii*) the axis $\simeq$ 10 Å can be likened to that in phillipsite where a more open crankshaft type of four-membered chain occurs. A framework meeting all these requirements is that shown in Figs. 3 and 4, which is proposed for Li-A(BW).

At first the space group was taken as the higher symmetric *Pnma* and a program which refined interatomic distances to prescribed values (henceforth called DLS, MEIER and VILLIGER, 1969) was used to refine the proposed framework, assuming equal numbers of Al and Si atoms in both ordered and random arrangement. However, the resulting refined framework had an unacceptably high discrepancy index (0.170 Å) as compared with that when other structures were similarly refined, such as faujasite (0.028 Å) and yugawaralite (0.024 Å). So it was concluded that the non-centrosymmetric $Pna2_1$ was more probable, and it indeed gave a suitably low value for the index (0.029 Å; all quoted values are based on the same weighting scale).

X-ray refinement

X-ray intensities were measured on a G.E. XRD-6 powder diffractometer and areas by planimeter. The program used was a modification of an existing program (MEIER, 1970) to cater for overlying diffractions, by aggregating their intensities in the least-squares process. Least-squares were based on intensities, and Lorentz, polarization and multiplicity factors included in the calculated values. X-ray form factors were taken from the *International tables* and semi-ionized states were used, interpolating where necessary. First results were encouraging and a Fourier synthesis showed in addition to framework atoms, a high peak which was attributed to a water molecule and so included in subsequent refinement.

Initially the occupancy of one of the Si,Al positions was allowed to float. This revealed an ordering of Si and Al enabling separate form factors to be used from here on. The least-squares was restarted and after a few cycles R, based upon uncorrected intensities, fell to 0.16. A second Fourier showed two shallow peaks, one on either side of the water molecule, which were taken to indicate the presence of Li^+.

Table 2. *Coordinates and temperature factors of Li-A(BW)*

	x	y	z	B	Occupancy
Al	0.1635	0.0723	0.2500	3.5 Å^2	0.91 Al, 0.09 Si
Si	0.3581	0.3778	0.2521	3.0	1
O(1)	− 0.0062	0.1657	0.2055	7.4	1
O(2)	0.2658	0.2515	0.1278	12.9	1
O(3)	0.1840	0.0129	0.5606	10.1	1
O(4)	0.1747	− 0.1046	0.0829	0.3	1
H_2O	0.5110	0.1053	− 0.2570	5.5	0.98
Li(1)	0.3125	0.1970	− 0.2600	4.0	0.64
Li(2)	0.1850	0.2714	− 0.2190	4.0	0.27

These were inserted in further calculations and occupancies of 0.64 and 0.27 were instrumental in reducing R to 0.132.

Further refinement did not bring about the expected improvement as the shifts of framework atoms were now small whilst the coordinates of the cations oscillated. The final coordinates appear in Table 2, and Table 3 gives principal interatomic distances and angles, while Table 4 gives observed and calculated x-ray intensities.

Table 3. *Interatomic distances and angles for the refined Li-A(BW) structure*

Al—O distances	Si—O distances	O—O in AlO_4	O—O in SiO_4
Al—O(1) 1.919 Å	Si—O(1) 1.464 Å	O(1)—O(2) 2.917 Å	O(1)—O(2) 2.477 Å
Al—O(2) 1.903	Si—O(2) 1.537	O(1)—O(3) 2.926	O(1)—O(3) 2.454
Al—O(3) 1.641	Si—O(3) 1.527	O(1)—O(4) 2.957	O(1)—O(4) 2.613
Al—O(4) 1.674	Si—O(4) 1.695	O(2)—O(3) 3.034	O(2)—O(3) 2.226
Mean 1.784	Mean 1.556	O(2)—O(4) 3.068	O(2)—O(4) 2.634
		O(3)—O(4) 2.576	O(3)—O(4) 2.784
		Mean 2.913	Mean 2.531

Cation water environment

H_2O—H_2O 3.04 Å	Li(1)—H_2O 2.18 Å	Li(1)—O(4) 1.81 Å	Li(2)—O(3) 2.38 Å
H_2O—O(1) 2.98	Li(1)—O(2) 2.05	Li(2)—H_2O 2.06	Li(2)—O(4) 2.03
H_2O—O(4) 3.33	Li(1)—O(3) 2.20	Li(2)—O(2) 1.93	Li(1)—Li(2) 1.46

Framework angles

Al—O(1)—Si 139°	Al—O(2)—Si 137°	Al—O(3)—Si 140°	Al—O(4)—Si 123°

Table 4. *Observed and calculated intensities*

h k l	I_{obs}	I_{calc}
1 1 0	1562	1509
2 0 0	256	274
2 1 0	292	280
0 1 1	529	542
0 2 0	67	70
1 1 1	13	39
2 1 1	38	51
2 2 0	14	19
3 1 0	1395	1313
1 2 1	1042	1044
2 2 1	39	45
1 3 0 3 2 0	84	46
0 0 2	296	313
4 1 0	36	28
2 3 0	4	7
0 3 1	85	93
1 1 2 3 2 1 1 3 1	176	227
2 0 2	26	40
4 1 1	13	50
4 2 0	29	33
2 3 1 2 1 2	79	93
3 3 0	4	1
1 2 2	10	26
0 4 0	68	73
1 4 0	9	7
4 2 1 5 1 0	24	34
2 2 2	5	1
3 1 2 3 3 1	97	122
2 4 0	12	3
4 3 0	21	1
5 2 0	10	11
3 2 2 1 3 2	23	28
2 4 1	7	33
4 1 2 4 3 1 3 4 0	162	117
2 3 2	5	13
5 2 1	9	15
6 0 0	102	92
3 4 1	9	20
4 2 2 5 3 0	9	7
0 1 3	32	30
1 5 0	3	5
4 4 0	9	13
0 4 2 6 2 0 2 0 3	38	52
1 4 2 5 3 1 5 1 2 2 5 0 2 1 3 0 5 1	101	78
1 5 1	5	20
1 2 3 4 4 1	74	103
2 5 1	18	5
5 2 2 2 2 3 3 5 0 3 1 3	110	67
6 3 0 5 4 0 7 1 0	16	17
0 3 3 3 5 1 6 0 2	55	68
1 3 3 3 2 3	102	87
6 3 1 6 1 2 5 4 1	9	22
7 2 0	7	1
4 5 0 4 1 3	26	26
5 3 2	17	2
2 3 3	15	28
1 5 2	1	1
1 6 0 4 4 2	24	24
6 2 2	23	2
7 2 1 4 5 1	31	37
4 2 3	1	1
2 6 0	8	3
6 4 0 3 3 3	10	19
7 3 0	6	3
2 6 1 8 1 0 6 4 1 3 5 2	54	37
5 4 2 7 3 1 7 1 2 2 4 3	33	38
0 0 4	8	7
8 0 1	6	1
5 5 1	7	3
5 2 3	8	9
1 2 4	7	4
0 5 3	6	1
2 6 2 8 3 0 2 2 4 6 4 2 3 1 4 7 4 1	30	21
3 7 1	7	1
6 5 2	4	1
7 5 1	5	9
6 6 0 0 4 4	18	7
7 2 3 8 4 1	8	13

Refinement of the ratio Al/(Si + Al)

As a further check upon the correctness of the proposed framework and as a test of the usefulness of the DLS program in resolving framework structures, the Al/(Si+Al) ratio was refined against observed x-ray intensities. If the amount of Al in a zeolite lattice varies between 0 and 50% it has been shown (Smith and Bailey, 1963) that the mean (Si,Al)—O distance varies between 1.61 and 1.68 Å, assuming random distribution. Idealized frameworks were obtained from the DLS

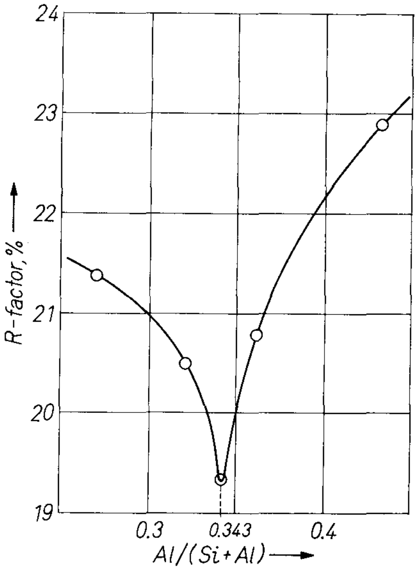

Fig. 5. X-ray intensity R factor plotted against Al/(Si + Al) ratio

program for distances in the permitted range and with the addition of water and cation positions previously described, were used to check with x-ray intensities. The resulting x-ray intensity R values were plotted against the amount of Al in the framework (Fig. 5), and showed a sharp minimum of 0.19 for a value of 0.343 in the ratio. The x-ray refinement of this framework converged with that already found.

Discussion

(a) General description

The framework is shown in Figs. 3 and 4 and consists of 4-, 6- and 8-membered rings. The 4-membered rings have one side in common and form ribbons or ladders of 5 Å repetition running along the length of the rods. Channels bounded by 8-membered rings also run parallel to the *c* axis, forming a one-dimensional set of free diameter 3.2 × 4.1 Å. Alternative ribbons are twisted in opposite senses so contracting the framework into one of the two most compact zeolites known. For comparison, densities in Si + Al per 1000 A^3 are: bikitaite 20.2, Li-A(BW) 19.0, analcime 18.6, etc.

Water molecules are found in the channel close to each other forming a column which touches O(3) of the framework. Two positions have been discovered for Li^+ occurring each side of the 6-membered ring and touching the water molecule. Both positions have partial occupancies distributed randomly, although it is unlikely that the closest pairs would both be occupied in view of the charge distribution. When greater allowance for positional errors is made, owing to the lightness of Li, it can be seen that both Li(1) and Li(2) touch O(2), O(3) and O(4), which are alternate oxygen atoms of the triangularly distorted 6-membered ring. The cation environment comprizing framework with water completing the sphere is similar to that already found in other zeolites (KERR and WILLIAMS, 1969).

(b) Formula

In a zeolite the aluminium in the framework has to be balanced by the cations to ensure electrostatic neutrality. The formula quoted by BARRER and WHITE shows too much Al_2O_3 for this to be so. This may be explained for it is known from electron microscopy, that their specimen was contaminated with amorphous gel and a few percent α eucryptite. Recently BORER (1969) has made a chemical analysis of one of his own preparations giving it the formula $LiAlSiO_4 \cdot H_2O$. Thus containing only one water molecule, which is undoubtedly correct as the structure described here can accommodate only one such molecule. In view of these considerations it is probable that the excess alumina and water in the formula by BARRER and WHITE, were in fact present as hydrated gel, and a more nearly correct formula would be $Li_{0.91}Al_{0.91}Si_{1.09}O_4 \cdot H_2O$.

(c) Aluminium in the framework

The chemical analysis of Li-A(BW), when adjusted as above, leads to an Al/(Si+Al) ratio of the order of 0.45, whilst tests with the DLS program and comparison of x-ray intensities lead one to expect a lower value of 0.34. This latter figure is well defined and does not vary to any extent with adjustments of water and cation. In the absence of more precise analysis and with only limited experience of the application of the DLS program, the actual value of Al/(Si+Al) remains unresolved.

It might be of advantage to future framework-type structure analyses in the powder field, if a program were available combining both distances and x-ray refinement. This would require rather a sophisticated weighting scheme in order to produce a framework having the best agreement with x-ray intensities subject to interatomic distances falling within a designated range.

Appreciable evidence has been found in favour of the ordering of Si and Al. Firstly by varying one occupancy as has been described above. Secondly, DLS refinement was carried out on random and ordered frameworks so that x-ray intensities could be compared. A drop in the x-ray *R* factor from 0.192 to 0.188 occurred when Si and Al were arranged in the manner already found. Finally further confirmation can be obtained from Table 3, where mean (Si,Al)—O distances are 1.78 and 1.56 Å for AlO_4 and SiO_4 tetrahedra respectively. These values are a little more widely spread than expected, probably due to the structure not being more fully refined. All things considered a tendency towards ordering is clearly exhibited.

(d) Exchange, sorption and comparison with other zeolites

Reports of the synthesis of A(BW) have all been in the presence of lithium, although once prepared the cation may readily be exchanged—partially at least—for another resulting in an observed swelling of the unit cell. Outgassed Li-A(BW) is known to absorb ammonia and nitrogen but only very limited quantities of propane. This is consistent with the estimated channel sizes.

Li-A(BW) shows a remarkable likeness to the mineral bikitaite $Li_2Al_2Si_4O_{12} \cdot 2H_2O$, where the analogy covers formula, compactness and framework. The refined structure of bikitaite is awaited with interest, but it is already known (MEIER, 1968, p. 16) to contain two-membered chains linked laterally in a way showing some similarity to Li-A(BW). Other comparisons may be made with cancrinite, equally of a fibrous habit, which possesses similar two-membered ribbons and frequently occurs under similar conditions of synthesis, save for a different cation. Also both phillipsite and gismondine show certain structural features in common with Li-A(BW).

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