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The structure of the synthetic zeolite (K,Ba)-G,*L*

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Auszug

Die Kristallstruktur des synthetischen Zeolites (K,Ba)-G,*L* bei Zimmertemperatur, mit einem Zellinhalt von $K_{2.7}Ba_{7.65}[Al_{18}Si_{18}O_{72}] \cdot 23H_2O$, wurde mittels genauer Pulverdaten bestimmt. Der Zeolith ist hexagonal mit den Gitterkonstanten $a = 18{,}70$ Å und $c = 7{,}50$ Å. Die Stuktur wurde unter der Annahme der Raumgruppe $P6/mmm$ bis zu einem $R(I)$-Wert von 0,13 verfeinert.

Das Alumosilikatgerüst von (K,Ba)-G,*L* ist demjenigen von Zeolith L sehr ähnlich. Die beiden Zeolithe haben jedoch verschiedene chemische Zusammensetzung. Sie unterscheiden sich sowohl im Si/Al-Verhältnis als auch in den Kationen, welche die Ladung des Gerüstes neutralisieren. Es sind drei Kationenpositionen gefunden worden, wovon sich nur eine im Hauptkanal befindet. Nur die Ionen im Hauptkanal können leicht ausgetauscht werden.

Abstract

The crystal structure of the synthetic zeolite (K,Ba)-G,*L*, of unit cell composition $K_{2.7}\,Ba_{7.65}\,[Al_{18}Si_{18}O_{72}] \cdot 23H_2O$, has been determined at room temperature from accurate powder data. The zeolite is hexagonal with $a = 18.70$ Å and $c = 7.50$ Å. The structure was refined to an $R(I)$ value of 0.13 assuming space group $P6/mmm$.

The aluminosilicate framework of (K,Ba)-G,*L* is very similar to that of zeolite L. However the chemical compositions of the two zeolites differ substantially, both in the Si/Al ratios and in the ions which neutralize the framework charge. Three cation positions were located but only one of these is in the main channel. Ions in the main channel are the only ones likely to exchange readily.

Introduction

In 1964 Barrer and Marshall reported the synthesis of a synthetic Ba zeolite, called Ba-G, which had no natural counterpart. Barrer and Mainwaring (1972) repeated this synthesis using

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metakaolinite with and without additional silica as starting materials, and also showed that the yield and purity of this species was increased when using a mixture of K and Ba hydroxides. They were able to index it on a hexagonal unit cell, similar to that of zeolite L (BARRER and VILLIGER, 1969a) and zeolite Ω (BARRER and VILLIGER, 1969b). But they pointed out that the intensities of this new species resembled those of zeolite L.

Despite the low silica/alumina ratio the zeolite has a high thermal stability. It also shows promising sorption properties (MAINWARING, 1970). Therefore it was thought interesting to confirm the proposed framework structure by an x-ray structure determination and if possible to locate the cations. To avoid ambiguity the species has been renamed (K,Ba)-G,*L*, where the letter *L* indicates that it has a framework similar to that in zeolite L.

Experimental

Chemical analysis of the sample used in this structure determination gave the following results:

$$(0.15\ K_2O,\ 0.85\ BaO)\ Al_2O_3 \cdot 2.14\ SiO_2,\ 2.6\ H_2O\,.$$

The measured density was 2.46 g/cm³. The hexagonal cell dimensions were determined by means of a Guinier photograph with Cu$K\alpha_1$ radiation and lead nitrate as an internal standard. The refined values are:

$$a = 18.701 \pm 0.002\ \text{Å},\ c = 7.501 \pm 0.001\ \text{Å}\,.$$

The above results lead to an average unit cell content of

$$K_{2.7}\ Ba_{7.65}\ [Al_{18}Si_{18}O_{72}] \cdot 23\,H_2O\,.$$

The x-ray powder pattern was obtained with a Philips PW 1050/25 powder diffractometer using Co$K\alpha$ radiation. A numerically controlled step-scan device, designed by M. T. FROST and D. WHITEHEAD of the Geology Department was used, which punched the output on paper tape. With the aid of a computer program partially overlapping peaks were resolved. Thus 147 lines were measured up to $2\theta = 90°$, 121 of which were clearly above background. For the least-squares refinement individual weights have been assigned to the intensities according to the counting rate and the degree of overlapping. No absorption correction was applied. For purpose of identification calculated spacings and relative intensities for Cu$K\alpha$ radiation are given in Table 1.

Table 1. *Spacings and relative intensities for* Cu$K\alpha$ *radiation of* (K,Ba)-G,*L*

h k l	d_{calc}	I_{rel}	h k l	d_{calc}	I_{rel}	h k l	d_{calc}	I_{rel}	h k l	d_{calc}	I_{rel}	h k l	d_{calc}	I_{rel}
1 0 0	16.196	100	3 1 1	3.854	7	5 0 1	2.974	2	0 0 3	2.500	< 1	3 0 3	2.269	-
1 1 0	9.350	4	0 0 2	3.750	2	2 2 2	2.926	31	1 0 3	2.471	5	6 2 0	2.246	< 1
2 0 0	8.098	< 1	3 2 0	3.716	2	5 1 0	2.909		6 1 0	2.470		4 4 1	2.232	14
0 0 1	7.501	16	1 0 2	3.654	2	3 1 2	2.879	5	5 0 2	2.451	8	7 0 1	2.211	3
1 0 1	6.806	3	4 0 1	3.563	< 1	3 3 1	2.872		5 2 1	2.451		5 3 1		
2 1 0	6.121	1	4 1 0	3.534	1	4 2 1	2.834	4	1 1 3	2.416	< 1	2 2 3	2.205	8
1 1 1	5.851	1	1 1 2	3.481	10	4 0 2	2.752	2	3 3 2	2.397	3	6 0 2	2.191	5
2 0 1	5.503	< 1	2 0 2	3.403	< 1	5 1 1	2.712	27	2 0 3	2.389	-	3 1 3	2.185	
3 0 0	5.398	3	3 2 1	3.329	16	6 0 0	2.699		4 2 2	2.371	1	4 3 2	2.171	< 1
2 1 1	4.743	7	5 0 0	3.239	19	4 3 0	2.662	2	6 1 1	2.346	1	6 2 1	2.152	-
2 2 0	4.675	3	2 1 2	3.198	10	3 2 2	2.639	10	4 4 0	2.338	4	7 1 0	2.145	-
3 1 0	4.492	< 1	4 1 1	3.197		5 2 0	2.593	1	2 1 3	2.315	3	5 2 2	2.133	-
3 0 1	4.382	3	3 3 0	3.117	26	4 1 2	2.572	-	7 0 0	2.314		4 0 3	2.127	1
4 0 0	4.049	1	3 0 2	3.080		6 0 1	2.540	2	5 3 0	2.314		3 2 3	2.074	1
2 2 1	3.968	46	4 2 0	3.061	4	4 3 1	2.509	5	5 1 2	2.298	2	5 4 0	2.074	

The material investigated was synthesized using as starting material a metakaolinite which contained some anatase as impurity. Therefore the intensity of the lines 410, 422, (513/810), 004, (404/703/533/910/650) and (623/642) had to be corrected approximately for overlap with anatase lines.

For purposes of Fourier synthesis, values of F_{obs} were assigned which were proportional to the calculated structure amplitudes (BROUSSARD and SHOEMAKER, 1960).

Determination and refinement of the structure

There are three framework structures or structure proposals which have approximately the cell dimensions of (K,Ba)-G,*L* and which also explain qualitatively the observed sorption properties. These are the frameworks of zeolite L (BARRER and VILLIGER, 1969a), the second proposal considered by these authors for zeolite L, and a third structure not considered at that time. In the present work this third structure was ruled out because the required extinctions were not observed.

For both the remaining proposals initial framework coordinates were calculated with the aid of the distances least-squares program DLS (MEIER and VILLIGER, 1969) using a mean (Si,Al)—O distance of 1.681 Å corresponding with the observed Si/Al ratio of 1. However, right from the start the refinement of the second proposal did not progress very well and it was soon evident that the structure of (K,Ba)-G,*L* must indeed be based on the L-type framework.

If one does not distinguish between Si and Al the highest possible symmetry for the L-type framework is $P6/mmm$. This space group was used during the whole structure determination. The first three-dimensional difference Fourier maps were based on the distance least-squares (DLS) framework coordinates and an overall temperature factor of 3.0 Å^2. They showed two rather high peaks Ba (1) and Ba (2). The first one is located in the cancrinite cage and the second midway between two adjacent cancrinite cages. In addition a somewhat smaller peak, later called (K, Ba), was found in the main channel, in front of the eight-membered ring. Including Ba (1) and Ba (2) as fully occupied and (K, Ba) as half occupied Ba positions reduced the *R(I)* value[1] from the relatively high initial value of 0.76 to 0.34. From further three-dimensional F_o and F_c maps shifts were calculated for positional parameters of the framework atoms and the occupancy factors of the cation positions were adjusted.

For reasons discussed later the determination of water positions proved to be difficult. Nevertheless, two fairly distinct peaks, I and II, were located near the cation position (K, Ba). They were included using the scattering factor of oxygen. Further difference and F_o maps showed a number of small additional peaks, most of them overlapping, nearer to the centre of the main channel. Instead of including all these positions with a low occupancy, it was decided to insert only the most relevant peaks and to allow their temperature factors to become rather high if necessary. This was thought to be justified since it helped to keep the number of parameters to a minimum without really limiting the information which it is possible to deduce from the available data. Thus only three further sites III, IV and V were included, the last of which disappeared during the course of the refinement. The least-squares refinement was then commenced with the aid of the ORFLS computer programme (Busing, Martin and Levy, 1967) adapted for powder data. The function minimized was:

$$r = \sum_j w_j \, (Y_o - Y_c)_j^2 ; \quad Y_c = \sum_i m_i \, Lp_i \, (sF_i)^2 ,$$

where w_j is the weighting factor and Lp_i is the Lorentz and polarisation factor. Since the cation position (K, Ba) had a comparatively low occupancy using the scattering factor of Ba^{2+}, it was concluded that

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[1] Defined as $R(I) = \Sigma |I_o - I_c| / \Sigma I_o$

where $I_c = \sum_{i=1}^{n} m_i \, (sF_i)^2$

n = number of non-equivalent reflections contributing to a powder line

m = multiplicity factor

sF = scaled calculated structure amplitude.

Table 2. *Parameters of hydrated* (K, Ba)-G,*L*
(estimated standard deviations are given in brackets)

Atom	Position based on *P*6/*mmm*	Fraction occup.[1]	*x*	*y*	*z*	*B* [2]
(Si, Al)(1)	12 *q*	1	0.0890(15)	0.3500(15)	1/2	0.3 Å^2
(Si, Al)(2)	24 *r*	1	0.1665(15)	0.4980(15)	0.2175(15)	0.6
O(1)	6 *k*	1	0	0.2675(35)	1/2	1.7
O(2)	6 *m*	1	0.1635(15)	0.3270	1/2	1.0
O(3)	12 *o*	1	0.2690(10)	0.5380	0.2765(40)	1.7
O(4)	24 *r*	1	0.0980(15)	0.4045(20)	0.3225(30)	2.2
O(5)	12 *o*	1	0.4315(15)	0.8625	0.2545(50)	7.0
O(6)	12 *p*	1	0.1540(25)	0.4825(25)	0	5.3
Ba(1)	2 *d*	1.0	1/3	2/3	1/2	4.1
Ba(2)	3 *g*	0.83	0	1/2	1/2	6.2
K, Ba [3]	6 *j*	0.73	0	0.3250(10)	0	5.1
I	6 *j*	0.85	0	0.1780(55)	0	11.0
II	6 *l*	0.95	0.1450(25)	0.2900	0	13.5
III	12 *n*	1.0	0	0.1455(30)	0.3420(50)	20.5
IV	12 *o*	0.40	0.1110(35)	0.2220	0.2090(150)	4.5

[1] Estimated standard deviation of the order of 0.02 and 0.1 for cations and sites I—IV respectively.

[2] Estimated standard deviation of 0.5—1.0 Å^2 for framework atoms and cations and 3.0—4.0 Å^2 for sites I—IV.

[3] Refined assuming a K/Ba ratio of 1.

Table 3. *Interatomic distances*
(estimated standard deviations in brackets)

(Si,Al)(1)—O(1)	1.61(0.03) Å	(Si,Al)(2)—O(3)	1.74(0.03) Å
(Si,Al)(1)—O(2)	1.65(0.02) Å	(Si,Al)(2)—O(4)	1.75(0.04) Å
(Si,Al)(1)—O(4)	1.64(0.02) Å	(Si,Al)(2)—O(5)	1.68(0.02) Å
		(Si,Al)(2)—O(6)	1.65(0.01) Å
mean	1.63 Å	mean	1.70 Å

		Coordination
Ba(1)—O(3)	2.67(0.04) Å	6-fold
Ba(2)—O(5)	2.89(0.04) Å	4-fold
Ba(2)—O(4)	3.40(0.02) Å	8-fold
(K,Ba)—O(6)	2.91(0.04) Å	2-fold
(K,Ba)—O(4)	2.95(0.02) Å	4-fold
(K,Ba)—I	2.74(0.1) Å	1-fold
(K,Ba)—II	3.09(0.02) Å	2-fold

Table 4. *Observed and calculated values of the corrected intensities of* (K,Ba)-G,*L*. $I_{\text{calc}} = \sum_{i} m_i \, (sF_i)^2$

h k l	I_c	I_o
1 0 0	131	128
1 1 0	5	17
2 0 0	6	1
0 0 1	101	96
1 0 1	25	25
2 1 0	7	7
1 1 1	12	10
2 0 1	8	4
3 0 0	35	34
2 1 1	102	102
2 2 0	48	44
3 1 0	0	6
3 0 1	46	48
4 0 0	0	17
2 2 1	1308	1033
3 1 1	179	173
0 0 2	38	41
3 2 0	59	63
1 0 2	64	66
4 0 1	11	9
4 1 0	20	25
1 1 2	310	305
2 0 2	9	20
3 2 1	569	529
5 0 0	656	649
2 1 2 4 1 1	361	340
3 3 0 3 0 2	916	996
4 2 0	168	172
5 0 1	93	100
2 2 2 5 1 0	1130	1364
3 1 2 3 3 1	226	223
4 2 1	181	164
4 0 2	78	81
5 1 1 6 0 0	1423	1411
4 3 0	58	108
3 2 2	501	524
5 2 0	46	53
4 1 2	16	< 5
6 0 1	106	107
4 3 1	259	294
0 0 3	7	19
1 0 3 6 1 0	315	315
5 0 2 5 2 1	461	496
1 1 3	44	32
3 3 2	170	193
2 0 3	0	< 6
4 2 2	22	52
6 1 1	57	57
4 4 0	122	267
2 1 3 7 0 0 5 3 0	246	237
5 1 2	189	187
3 0 3	32	< 5
6 2 0	2	46
4 4 1	1102	1104
7 0 1 5 3 1	195	250
2 2 3	717	641
6 0 2 3 1 3	476	412
4 3 2	41	30
6 2 1	11	< 6
7 1 0	11	< 6
5 2 2	7	< 6
4 0 3	60	69
3 2 3 5 4 0	97	87
6 1 2 7 1 1	374	337
4 1 3 6 3 0	58	42
8 0 0	18	20
5 4 1	23	25
4 4 2 5 0 3 7 2 0	124	80
7 0 2 5 3 2 6 3 1	280	311
8 0 1 3 3 3	108	88
4 2 3	2	< 13
6 2 2	9	< 13
7 2 1	129	79
5 1 3 8 1 0	336	196
0 0 4	798	702
5 5 0	100	166
1 0 4 7 1 2 6 4 0	168	148
1 1 4 8 1 1 6 0 3	261	253
2 0 4	13	57
4 3 3 7 3 0	7	33
5 4 2 5 5 1	41	< 15
6 4 1 5 2 3 9 0 0	658	594
2 1 4 6 3 2	275	255
8 0 2	40	82
3 0 4 7 3 1 8 2 0	123	107
6 1 3	167	149
7 2 2 9 0 1	448	363
2 2 4	6	< 10
3 1 4	17	27
8 2 1	1144	1113
4 4 3	21	83
4 0 4 7 0 3 5 3 3 9 1 0 6 5 0	665	606
8 1 2	38	139
7 4 0	33	31
3 2 4 5 5 2	39	43
6 2 3 6 4 2	84	91
4 1 4 9 1 1 6 5 1	187	223
8 3 0	62	64
7 3 2 7 4 1	65	40
7 1 3	74	207
5 0 4 9 0 2 10 0 0	495	500
3 3 4 8 3 1	33	29
4 2 4 8 2 2	849	926
5 4 3 9 2 0	91	340
10 0 1 6 3 3 5 1 4 8 0 3	365	357
9 2 1 6 6 0	1354	1367
7 2 3 7 5 0	416	480
9 1 2 6 5 2	356	473
6 0 4 10 1 0	928	934
4 3 4 7 4 2 8 4 0 6 6 1	46	62
5 2 4 7 5 1	183	160
8 1 3	51	< 14
8 3 2 10 1 1	60	43
0 0 5 8 4 1 5 5 3 9 3 0	154	92
1 0 5 6 1 4 6 4 3	250	196
10 0 2	12	< 15
1 1 5	4	< 15
2 0 5	7	< 15
7 3 3 11 0 0	67	< 15
9 2 2 9 3 1	57	56
4 4 4	1	< 15
9 0 3	18	< 15
2 1 5 7 0 4 5 3 4 10 2 0	78	94
3 0 5 11 0 1 8 2 3	563	485
6 2 4 6 6 2 7 6 0	49	122
7 5 2 2 2 5 10 2 1 8 5 0 3 1 5 10 1 2	583	492
8 4 2	41	< 16
7 1 4 7 6 1	7	< 16
4 0 5 9 1 3 6 5 3 11 1 0 9 4 0 8 5 1	492	564
7 4 3 3 2 5 5 4 4 9 3 2	650	627
4 1 5 6 3 4 9 4 1 11 1 1	88	126
8 0 4 8 3 3 10 3 0 11 0 2	123	81
5 0 5 7 2 4	29	< 19
10 0 3	83	< 20
10 2 2	34	< 20
3 3 5 10 3 1 12 0 0 4 2 5 9 2 3 7 6 2	1227	1252
11 2 0 7 7 0 5 1 5 8 1 4 8 5 2 8 6 0	285	177
12 0 1	69	65
5 5 4 6 6 3 6 4 4 7 5 3 9 5 0 9 4 2 11 1 2 11 2 1 7 7 1 6 0 5 8 6 1 10 1 3 4 3 5 7 3 4 8 4 3	1159	1183
5 2 5 9 0 4 9 5 1 10 4 0	184	192
12 1 0	49	71
10 3 2	105	63
8 2 4	7	< 21
9 3 3	39	< 21
6 1 5	1	< 21
10 4 1	401	617
12 1 1	37	21
12 0 2 11 0 3 11 3 0	58	86

most of the K^+ must be accommodated in this position. During the final least-squares cycles a mixed scattering factor was therefore used, corresponding to a K/Ba ratio of 1. The refinement finally stopped at the *R(I)* value of 0.13 for the observed reflections, which corresponds with a conventional *R(F)* value of 0.10. A final difference Fourier map showed no significant peak.

The final atom parameters with their estimated standard deviations are shown in Table 2. Those interatomic distances which are of interest are assembled in Table 3. Lastly, Table 4 contains the calculated and observed values for the corrected intensities.

Results and discussion

Framework

Although the L-type framework has been described in detail elsewhere (BARRER and VILLIGER, 1969a; MEIER and OLSON, 1971) a stereoscopic drawing is presented in Fig. 1. It shows clearly how the columns consisting of cancrinite cages joined by bridges of six oxygen atoms are linked to form the large main channel with its twelve-membered ring windows. Since the sample of (K,Ba)-G,*L* examined

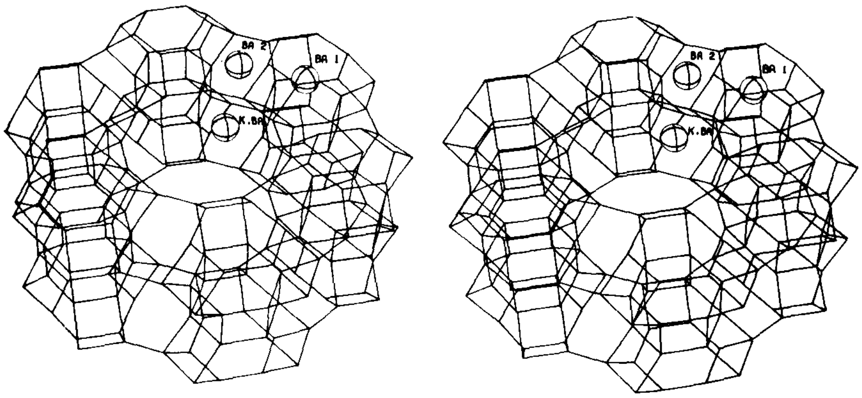

Fig. 1. Stereoscopic drawing of the framework structure of (K,Ba)-G,*L*. (Si,Al) atoms are centred at the apices, oxygen atoms are not shown. Also indicated are the three cation sites

is more aluminous than zeolite (Na,K)-*L*, its *a* cell dimension is increased by 0.3 Å. Apart from this, no significant differences were found between the two framework structures. This was anticipated because the framework is fairly rigid.

The overall mean (Si,Al)—O distance was found to be 1.67 Å. Within the limits of error, this is in agreement with the expected value of 1.681 Å for a Si/Al ratio of 1 (RIBBE and GIBBS, 1969). However, the (Si,Al)—O distances of the (Si,Al)(1) tetrahedra are significantly shorter and this might suggest a concentration of Si in the twelve-membered ring. This would be similar to the conclusion GARD and TAIT (1972) drew in their discussion of the structure of offretite. Offretite possesses the same columns of cancrinite cages joined by six oxygen bridges as in zeolite L. But such a conclusion is not possible in the present case. According to LOEWENSTEIN's rule (1954) Si and Al have to alternate in a framework with a Si/Al ratio of 1. It is therefore most likely that these shortenings of the (Si/Al)—O distances are due to symmetry restrictions and averaging by the assumed high symmetry. The restrictions are more severe for the atoms in the twelve-membered ring than they are for the atoms in the hexagonal prisms.

Cations

Three different cation sites were located. They are shown in Fig. 1. Position Ba(1) in the centre of the cancrinite cage is fully occupied by Ba^{2+} ions. On the other hand, position Ba(2), midway between the centres of two adjacent cancrinite cages was found to have only fractional occupancy. This could of course mean that some K^+ ions also occupy this position. However, most of the 2.7 K per unit cell indicated by the chemical analysis are thought to be located in the position (K, Ba), in front of the boat-shaped eight-membered ring. This is the only cation position that lies in the main channel and which is therefore exchangeable. It was refined assuming a K/Ba ratio of 1 and a final fractional occupancy factor of 0.73 was obtained. On the above assumption this corresponds with 2.2 K^+ per unit cell.

All the three cation positions described have also been found in zeolite L. They account in terms of electrons for 87% of the cations found by chemical analysis. The remaining cations (corresponding approximately with one Ba^{2+} per unit cell) are probably distributed in the main channel. In contrast to zeolite (Na, K)-L (BARRER and VILLIGER, 1969a) and natural offretite (GARD and TAIT, 1971) no scattering matter was found in the hexagonal prism. The shortest distances between cations and framework oxygen atoms are listed in Table 3. They compare favourably with Ba—O distances found in other Ba aluminosilicates such as celsian (NEWNHAM and MEGAW, 1960) and harmotome (SADANAGA, MARUMO and TAKÉUCHI, 1961). In these structures the ranges of Ba—O distances are 2.67 Å—3.14 Å and 2.77 Å —3.26 Å respectively.

Zeolitic water

As mentioned earlier, the determination of meaningful water positions was not possible. The main reasons for this are as follows. It appears that the larger the cavities and channels of zeolites, the less fixed are the water molecules at particular positions. The water becomes more fluid-like the further away it is from the framework. Accordingly, GRAMLICH (1971), for example, found it very difficult to locate and refine meaningful water positions in the main channel of natural mordenite. At the same time, it is likely that the arrangement of the water molecules does not possess the high symmetry assumed for the refinement of the framework. This would also result in smearing out some positions. In addition, the partial occupancy of position (K, Ba) suggests that the arrangement of the water positions may vary depending on the presence or absence of a cation. For these reasons the refined water positions, especially the sites III and IV, cannot be taken as accurately representing the locations of fixed water molecules. To give some idea, however, of the water distribution

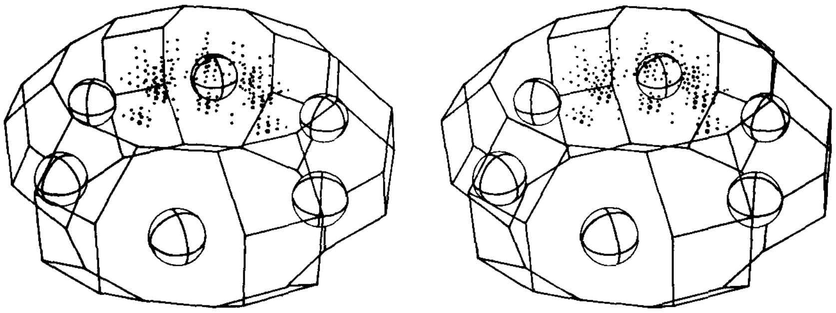

Fig. 2. Electron distribution in the main channel. The radii of the black circles are proportional to the electron density. The cation position (K, Ba) is also shown

a stereoscopic drawing of the electron density in the main channel is given in Fig. 2. The F_o map for this figures was calculated using the final coordinates.

Si,Al distribution

It has been noted earlier that the true symmetry of (K, Ba)-G,*L* must be lower than $P6/mmm$. The ratio between the number of observations and the number of variables was 2.8 (3.3 when including unobserved reflections) which would only just allow a symmetry reduction of the order of 2. On the other hand an ordered Si/Al distribution would not only require a reduction in symmetry but also a doubling of the *c* cell constant. However no evidence was found in the powder pattern for a doubled unit cell.

It is interesting to note, that while (Na, K)-L crystallizes with a Si/Al ratio of 2.5—3.5 (Breck and Flanigen, 1967), (K, Ba)-G,*L* can evidently form with a ratio of 1. This behaviour can perhaps be explained by the total number of cation sites available. These are the three positions already discussed totalling 11 per unit cell plus a possible position in the centres of the hexagonal prisms which adds two more. Therefore in an L-type structure having 36 (Si, Al) tetrahedra per unit cell and containing only monovalent cations (e.g. Na, K) the minimum Si/Al ratio would be 1.8. Since it is often found that cation positions in zeolites are only partially occupied it is expected, and observed, that the ratio Si/Al can exceed 1.8. On the other hand when divalent ions (e.g. Ba) are present as in (K, Ba)-G,*L*, although no hexagonal prism sites were occupied, the remaining 11 positions per unit cell easily allow for Si/Al ratios from 1 upwards.

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