

Acta Cryst. (1969). B25, 2161

The crystal structure of KBF_4 * By GEORGE BRUNTON, *Reactor Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830, U.S.A.*

(Received 13 March 1969)

The crystal structure of KBF_4 is isostructural with that of KClO_4 and the B-F bond distances (1.378 to 1.391 Å) are almost identical to those published for NaBF_4 .

Introduction

The crystal structure of the low temperature polymorph of KBF_4 is isostructural with that of KClO_4 and the lattice parameters $a_0 = 8.6588 \pm 0.0005$, $b_0 = 5.4800 \pm 0.0004$, $c_0 = 7.0299 \pm 0.0008$ Å at 24°C are in better agreement with the KClO_4 lattice parameters (Mani, 1957) than those previously published for KBF_4 by Ballanca & Sgarlata (1951) and Pesce (1930). The calculated density is 2.5067 g.cm⁻³ and $Z=4$.

The crystal structure of KBF_4 has been refined as part of the basic research on the properties of alkali metal fluoroborates, mixtures of which are being investigated as molten salt coolants for nuclear breeder reactors (ORNL, 1967).

Experimental

Euhedral crystals of KBF_4 were grown from a saturated solution of purified KBF_4 and HF in water. The crystals

* Research sponsored by the U.S. Atomic Energy Commission under contract with Union Carbide Corporation.

were prepared by L. O. Gilpatrick of the Reactor Chemistry Division and a chemical analysis of the crystals gave (in weight per cent): K, 30.9; B, 8.66; F, 60.3; H_2O , 0.20; theoretical: K, 31.06; B, 8.59; F, 50.38. The crystals contain 210 ppm of oxygen as measured by BrF_3 displacement. The oxygen is probably present as OH^- .

A small crystal $0.145 \times 0.139 \times 0.323$ mm bounded by the forms $\{101\}$ and $\{210\}$ was mounted on a Picker four-circle goniostat, and the reflection intensities were measured with a scintillation-counter detector using unfiltered $\text{CuK}\alpha$ radiation. Independent reflections out to $2\theta = 145^\circ$ were measured by the 2θ scan technique (Busing, Ellison, Levy, King & Roseberry, 1968).

The conditions for reflection are: hkl , no conditions; $0kl$, $k+l=2n$; and $hk0$, $h=2n$; consistent with $Pnma$ (No. 62) and $Pna2_1$ (No. 33). The lattice parameters were determined by least-squares adjustment from 31 Mo $K\alpha_1$ reflections (Mo $K\alpha_1 = 0.709260$ Å).

The structure was refined by iterative least-squares with a modification of the Busing, Martin & Levy (1962) computer program. The starting parameters were the centrosymmetric set suggested by Wyckoff (1965) and the results

Table 1. *Atomic parameters for KBF_4*

The number in parentheses is the standard error in terms of the last significant digit, as derived from the variance-covariance matrix.

	$x10^4$	$y10^4$	$z10^4$	$\beta_{11}10^4$ *	$\beta_{22}10^4$	$\beta_{33}10^4$	$\beta_{12}10^4$	$\beta_{13}10^4$	$\beta_{23}10^4$
K	1844.9 (7)	2500	1611 (2)	37 (2)	183 (5)	116 (3)	0	-1.4 (8)	0
B	626 (4)	2500	6897 (7)	38 (5)	142 (12)	111 (9)	0	-9 (5)	0
F(1)	1789 (3)	2500	5560 (4)	110 (4)	287 (9)	153 (7)	0	50 (4)	0
F(2)	-814 (3)	2500	6049 (5)	75 (4)	385 (11)	245 (7)	0	-71 (4)	0
F(3)	774 (2)	440 (3)	8039 (3)	92 (3)	173 (6)	165 (5)	-1 (3)	8 (2)	42 (4)

* Coefficients in the temperature factor: $\exp [-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

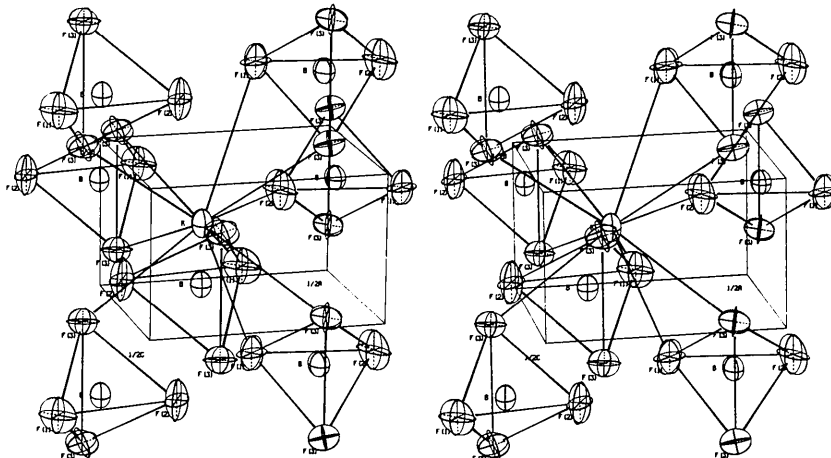


Fig. 1. A stereoscopic drawing of the structure of KBF_4 . One fourth of a unit cell is outlined.

Table 2. The interatomic distances and F-B-F angles for KBF₄

The number in parentheses on the interatomic distances is $\sigma \times 10^4$ and on the angles $\sigma \times 10$.

K-F(2)	2.758 (3) Å	K-F(1)	2.776 (3) Å
2[K-F(3)]	2.793 (2)	2[K-F(3)]	2.803 (2)
2[K-F(3)]	2.905 (2)	2[K-F(1)]	3.075 (2)
B-F(1)	1.378 (5)	B-F(2)	1.382 (4)
2[B-F(3)]	1.391 (3)	2[F(1)-F(3)]	2.255 (3)
F(1)-F(2)	2.280 (4)	2[F(2)-F(3)]	2.263 (3)
F(1)-B-F(2)	111.4 (4)°	2[F(1)-B-F(3)]	109.0 (2)°
2[F(2)-B-F(3)]	109.4 (2)	F(3)-B-F(3)	108.5 (4)

Table 3. Observed and calculated structure factors $\times 10$ for KBF₄

L	F ₀ B ₀	FCAL	L	F ₀ B ₀	FCAL	L	F ₀ B ₀	FCAL	L	F ₀ B ₀	FCAL	L	F ₀ B ₀	FCAL	L	F ₀ B ₀	FCAL		
0	0	0	7	133	-148	4	26	26	6	46	44	3	362	-353	0	25	29	2	
2	505	-383	1	2	148	5	237	-243	7	131	-136	4	25	33	1	131	-130	3	
4	254	-246	1	280	282	6	185	-193	3	1	1	5	320	-325	2	11	2	4	
6	643	232	2	445	456	7	80	84	1	148	-149	6	38	-39	6	5	10	5	
0	1	1	1	119	-119	2	2	2	2	419	424	7	180	196	1	110	110	6	
1	62	52	4	241	-249	0	444	454	3	48	-51	4	4	1	2	340	326	7	
3	220	218	5	82	85	1	496	500	4	120	-120	0	535	513	3	230	-231	0	
5	294	313	6	89	91	2	189	-177	3	113	115	1	72	-75	4	77	0	6	
7	63	-70	7	120	-127	3	78	-70	6	10	2	2	109	110	5	51	-51	1	
0	524	-581	1	51	51	4	248	-241	3	56	55	3	5	1	4	238	-240	5	
2	259	-231	2	410	418	6	133	130	1	83	79	5	5	-7	1	66	-60	4	
4	310	311	3	244	-246	7	54	56	2	79	-74	6	86	83	2	251	-253	5	
6	0	112	4	182	-185	2	3	3	3	393	-377	7	9	1	3	194	-182	6	
0	3	0	5	11	-10	0	110	114	4	220	-219	0	4	2	4	152	154	7	
1	346	350	5	72	72	1	129	-132	5	118	115	0	35	31	5	82	81	6	
3	247	-231	1	4	4	1	172	165	1	34	-34	4	45	-46	2	112	-109	3	
5	271	-269	1	37	-35	3	42	-39	3	109	106	2	89	90	6	5	2	32	
0	4	0	4	212	-219	4	60	-54	3	3	3	3	1	207	-210	2	149	151	1
2	56	590	1	107	-107	2	3	3	3	3	3	3	3	3	3	3	3	3	3
4	148	-149	4	90	86	6	107	103	2	231	-234	5	274	266	3	417	404	4	
6	125	-122	5	73	72	2	4	4	3	249	240	6	18	0	4	116	-113	5	
0	137	130	1	81	-85	4	107	-107	4	85	80	4	4	3	5	132	-126	6	
1	71	73	2	63	-64	2	26	-23	6	16	16	1	45	-44	7	82	-79	0	
3	21	-24	3	224	227	3	72	-73	3	3	3	2	103	104	1	5	3	1	
5	138	135	4	45	-40	8	83	1	1	63	-58	2	60	1	25	26	2		
7	6	6	5	73	-67	5	159	159	2	161	163	4	160	158	2	106	104	3	
0	237	-258	1	6	1	5	0	0	3	244	236	5	23	22	3	250	235	4	
2	54	57	2	135	130	1	204	223	5	31	-32	12	121	-121	4	156	-153	8	
4	103	96	3	39	41	2	142	146	6	6	-5	0	25	-20	5	129	-127	6	
6	1	1	3	44	44	0	4	4	4	4	4	4	4	4	4	27	-28	6	
1	81	-79	0	32	-10	4	30	27	1	45	-43	1	263	252	1	84	88	1	
3	332	-319	0	90	86	5	125	-116	2	173	181	2	17	16	2	131	126	2	
5	382	-364	1	196	-185	2	6	6	3	23	23	3	135	-129	3	180	-182	3	
7	5	5	2	266	265	3	241	-231	0	75	82	4	81	-78	4	21	15	4	
0	10	10	4	195	132	1	70	69	5	10	-10	5	193	-182	5	20	16	5	
2	25	21	5	258	253	3	21	-13	3	6	6	1	17	-13	1	5	5	1	
4	1	1	7	88	-88	3	7	8	1	47	46	0	4	5	1	12	-6	0	
6	151	-161	7	56	50	1	3	0	2	59	-58	0	111	108	2	159	-163	1	
8	370	390	2	1	1	55	-56	3	143	-137	1	95	-44	3	68	-61	2		
1	440	464	0	180	-175	2	510	480	4	0	0	2	77	76	4	126	122	0	
3	27	-23	1	407	407	3	410	397	0	331	-308	3	7	2	0	6	0	1	
5	72	75	2	194	196	4	200	-193	1	552	518	4	116	-117	0	52	-50	1	
7	26	21	3	38	-38	5	95	-91	2	71	74	4	4	6	1	58	-59	2	
9																330	-356	6	

are listed in Table 1. Scattering factors for K, B, and F were taken from Cromer & Waber (1965). The quantity minimized by the least-squares program was $\sum w_i |F_o^2 - |F_c^2||^2$ with weights, w_i , equal to the reciprocals of the variances which were estimated from the empirical equation:

$$\sigma^2(F_o^2) = [T + B + (0.05(T - B))^2] / [A(Lp)^2]$$

where T = total counts, B = background counts, A = absorption correction ($\mu = 15.6 \text{ cm}^{-1}$ for Cu $K\alpha$), and Lp = Lorentz and polarization (Brown & Levy, 1964). Anisotropic temperature factors were calculated for all atoms. A stereoscopic drawing of one K atom and its BF₄ nearest neighbors is shown in Fig. 1.

The discrepancy indices are

$$R_1 = \sum |F_o^2 - |F_c^2|| / \sum |F_o^2| = 0.0682$$

and $R_2 = \sum |F_o - |F_c|| / \sum |F_o| = 0.0384$, for 348 independent reflections. The standard deviation of an observation of unit weight, $[\sum w(F_o - F_c)^2 / (n_o - n_v)]^{1/2}$, is 1.878 where n_o is the number of reflections and n_v the number of variables. The interatomic distances and F-B-F angles are listed in Table 2 and the observed and calculated structure factors are listed in Table 3. An extinction correction was made on F_o by the method suggested by Zachariasen (1967).

The K⁺ ion is coordinated by 8F⁻ ions at distances less than 3.0 Å and by two more F⁻ ions at 3.075 Å. The K⁺ polyhedron shares edges with three and corners with four B-F₄ tetrahedra. The B-F₄ tetrahedra are slightly irregular with tetrahedral angles of 108.5° to 111.4° and B-F distances 1.378 to 1.391 Å, Table 2. The B-F distances are

almost equal to the B-F distances for NaBF₄ (1.386 and 1.392 ± 0.002 Å) found by Brunton (1968) from a refinement of the NaBF₄ structure proposed by Weiss & Zahner (1967). A calculated B-F single bond distance is 1.37 Å (Pauling, 1960).

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