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The Crystal Structure of K_3SiF_7

By D. L. Deadmore and W. F. Bradley

Illinois State Geological Survey, Urbana, Ill., U.S.A.

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A fine-grained homogeneous powder of composition K_3SiF_7 results from dry ignition of K_2SiF_6 to about 700 °C. Analysis of the powder data establishes that K_3SiF_7 is tetragonal with $a=7{\cdot}740$, $c=5{\cdot}564$ Å. A calculated powder diffraction diagram for a structure in $P4/mbm\text{–}D_{4h}^5$ agrees with the observed diagram with average departures less than 30%. The structure is a tetragonal honeycomb of composition K_2SiF_6 which adducts strings of alternating K and F ions.

A previous investigation by one of us (Deadmore, 1960) of the thermal stability of K_2SiF_6 in dry air revealed that at temperatures of 700 to 750 °C. it loses SiF_4 until the composition K_3SiF_7 is reached.

The K_3SiF_7 used here was prepared by heating K_2SiF_6 in dry air for 2 hr. at 750 °C. A chemical analysis gave 41·4% K, 10·2% Si, and 47·4% F, which agrees well with the calculated composition of 42·0% K, 10·2% Si, and 47·8% F. The measured density was 2·86 g.cm.$^{-3}$, and the calculated density, using the cell constants given below and $Z=2$, is 2·78 g.cm.$^{-3}$.

The product is fine-grained, and affords only a powder diffraction diagram, but inspection of the data suggests isomorphism with the $(NH_4)_3SiF_7$ crystal analyzed by Hoard & Williams (1942). Powder lines were all found to be indexable on the basis of a tetragonal cell with $a=7{\cdot}740$ and $c=5{\cdot}564$ Å (both ± about 1/20 of 1%), with $a/c=1{\cdot}391$, and a trial structure in $P4/mbm\text{–}D_{4h}^5$ afforded reasonable interatomic distances. The crystallization has a large temperature amplitude, and complete $\alpha_1\text{–}\alpha_2$ resolution is not realized within the range of unambiguous indexing. The accuracy estimate for lattice parameters is based on the absence of significant drift in calculated values between 50° and 70° 2θ with Cu radiation.

The disadvantage of being confined to powder data was in part offset by the advantage that the scattering power of potassium substantially exceeds that of the other constituents, with the result that some large index lines were probably properly indexed to d values as small as 0·889 Å.

Table 1. *Atom parameters for* K_3SiF_7 *in* $P4/mbm$*

$2K_I$	in	$2(a)$	$0, 0, 0;\ \frac{1}{2}, \frac{1}{2}, 0$
$4K_{II}$	in	$4(h)$	$x, x+\frac{1}{2}, \frac{1}{2}$, etc. with $x=0{\cdot}205$
$2Si$	in	$2(d)$	$0, \frac{1}{2}, 0;\ \frac{1}{2}, 0, 0$
$2F_I$	in	$2(b)$	$0, 0, \frac{1}{2};\ \frac{1}{2}, \frac{1}{2}, \frac{1}{2}$
$4F_{II}$	in	$4(g)$	$x, x+\frac{1}{2}, 0$, etc. with $x=0{\cdot}155$
$8F_{III}$	in	$8(k)$	$x, x+\frac{1}{2}, z$, etc. with $x=0{\cdot}390$ and $z=0{\cdot}216$

* Correspondence with the Hoard & Williams analysis is effected by the substitution $x=-x$.

Variable parameters are most sensitive to intensities of the reflections for which $h+k$ is odd. Fourteen of these were observed, resolved from neighboring features, among reflections up to $\sin\theta/\lambda=0{\cdot}5$, and five more fell at positions where lines could have been observed if present. The parameters selected in Table 1 are those affording apparent best agreement under an assumption that the six SiF_6 octahedral distances were equal. After application of an arbitrary temperature factor, they give average departures of $|I_o-I_c|/I_o$ of 0·28 (comparable with a reliability factor of about 0·15) for the 14 observations, and calculated intensities for the 5 possibilities not found or doubtful, were all trivial. Eight other $h+k$ odd reflections fell in mutual doublets, for which intensity sums show adequate agreement.

Table 2. *Summary of powder diffraction data for* K_3SiF_7

d_c (Å)	d_o (Å)	*hkl*	Integrated diffractometer count	I_o = Scaled relative count / Lorentz & polarization	F_o calc.	$F = F_o \exp -2 (\sin\theta/\lambda)^2$	$I_c = pF^2/100$	$(I_o - I_c)/I_o$	
5·564	5·60	001	1200	7·7	+19	18·6	6·9	+0·10	
5·474	5·52	110	3700	25	−26·3	25·8	27	−0·08	
3·903	3·92	111	2200	29	−16·1	15·5	20	+0·31	
3·870	3·88	200	1200	16	+15·8	15·3	9·4	+0·41	
3·462	3·48	210	1800	34	+16·6	16	20	+0·41	
3·177	3·19	201	17650	380	+78·3	74	445	−0·17	
2·940	2·95	211	1750	45	−16·2	15·3	37	+0·36	
2·782	2·792	002	5500	160	+95·4	90	162	−0·01	
2·737	2·746	220	9100	275	+106	100	400	−0·45	
2·480	2·488	112	2400	89	+35·3	32·6	85	+0·05	
2·456		221			−1		0·1		
2·448	2·455	310	5200	198	+61·6	57	260	−0·31	
2·259		202	(50)	(2)	−4·0	3·7	1		
2·240		311			+0·1		—		
2·169	2·174	212	10600	525	+69	62	615	−0·17	
2·146	2·152	320	2700	139	+51	46	170	−0·22	
2·003	2·007	321	400	25	−13·6	12	23	+0·08	
1·951	1·955	222	6250	404	+86·6	76	464	−0·15	
1·935	1·938	400	300	20	+18	16	10	+0·50	
1·877	1·880	410	2880	204	−60·4	52·5	222	−0·09	
1·855		003	(50)	(4)	−19·1	16·7	5·5		
1·838	1·839	312	900	67	+22·4	19·4	61	+0·09	−0·29
1·828		401			−11·0	9·6	7		
1·824	1·825	330	270	20	−38·3	33	44	−1·20	
1·779	1·781	411	1660	133	+26·4	22·5	81	+0·43	
1·757		113	(30)	(4)	+6·8	5·7	2·7		
1·733		331			+1·9	1·6	0·2		
1·731	1·732	420	570	49	+31	26	55	−0·12	
1·700	1·702	322	240	21	−17	14	32	−0·52	
1·672	1·673	203	1830	173	+54·4	45·3	165	+0·05	
1·653	1·654	421	1900	184	+47·9	40	255	−0·39	
1·635		213			+4·3	3·5	2		
1·589	1·590	402	2700	290	+78·6	64	333	−0·15	
1·556	1·557	412	940	108	−38·2	31	155	−0·43	
1·548	1·547	430	(30)	(5)	+12	9·7	7		
1·535		223			0·4		7		
1·526	1·526	332	280	33	−19	15	18	+0·45	−0·09
1·519		510	100	12	+24·5	19·5	31	−1·58	
1·491	1·493	431	860	106	−28·8	23	85	+0·20	
1·478	1·480	313	110	14	−10·1	8	10	+0·28	
1·470	1·471	422	1200	150	+38	30	142	+0·05	
1·465		511	(30)	(6)	+11·2	9	13		
1·437		520			−1·6	1·2	0·1		
1·403	1·404	323	750	109	−32·2	25	100	+0·08	
1·392	1·391	521	1100	164	+15·0	11·5	21	−0·09	
1·191		004			+115·4	89	158		
1·368	1·368	440	560	87	+80·4	61	150	−0·72	
1·353	1·352	432	430	68	+29·2	22·2	79	−0·16	
1·348		114			−7·9	6	3		
1·339		403			+15·6	11·9	11		
1·332	1·331	512	500	81	−19·7	14·9	35	−0·44	
1·329		441			+32·0	24	47		
1·327		530			+27·7	20·9	35		
1·319	1·319	413	620	103	+28·0	21·0	71	+0·31	
1·309	1·31	204	(20)		+7·6	5·7	2·5		
1·301		333			+7·9	5·9	2·8		
1·291	$1{\cdot}290_8$	531	1230	217	−31·3	23·2	86	+0·30	
1·291		214			+17·8	13·2	28		
1·290		600			+41·2	30·5	37		
1·277	1·273	522	400	74	+17·3	12·7	26	−0·46	
1·272		610			+43·7	32·1	82		
1·265	1·266	423	700	129	+44·6	32·5	170	−0·32	
1·257	1·257	601	(40)		+25·9	19	28		
1·240	1·241	611	1330	254	−35·5	25·6	104	−0·13	
1·240		224			+66·4	47·8	182		
1·228	1·226	442	400	79	+29·0	20·7	34	+0·18	
1·224		620			+27·4	19·5	31		

Table 2 (*cont.*)

d_c (Å)	d_o (Å)	*hkl*	Integrated dif-fractometer count	I_o= Scaled relative count / Lorentz & polarization	F_o calc.	$F = F_o \exp -2 (\sin\theta/\lambda)^2$	$I_c=pF^2/100$	$(I_o-I_c)/I_o$
1·209	1·210	314	300	60	+30·5	21·6	75	−0·28
1·209		540			−7·0	5	2	
1·198	1·197	532	850	177	+48·6	34·2	187	−0·28
1·195		621			+23·5	15·8	40	
1·188	1·187	433	240	51	−17·2	12	23	+0·22
1·181		541			−14·6	10·2	17	
1·175		513			−5·8	4	3	
1·170	1·168	602	1040	224	+64·9	44·8	160	+0·09
1·167		324			+24	16·5	44	
1·157	1·157	612	200	44	+15·6	10·7	18	+0·59
1·154		630			−5·5	4	1	
1·136	1·136	523	70	16	+18·3	12·4	25	−0·56
1·130	1·1295	631	440	102	+24·6	16·6	44	+0·08
1·129		404			−26·3	17·7	50	
1·120	1·118	622	680	156	+30·4	20·4	66	−0·15
1·118		414			−39·9	26·7	114	
1·113		005	(20)	(5)	+23·3	15·5	5	
1·109		542			−1·5	1	0·2	
1·106	1·106	334	90	21	−24·9	16·5	22	−0·05
1·101		443			+11·9	8	5	
1·095	1·095	550	130	30	−43·9	29	33	−0·23
1·095		710			+10·1	7	4	
1·090	1·090	115	80	19	−25·5	16·7	22	−0·16
1·084	1·084	424	170	40	+24·6	16·1	41	+0·02
1·079	1·079	533	280	67	−18·9	12·4	24	+0·64
1·074	1·073	551	450	107	+24·7	16	21	+0·13
1·074		711			−16·3	10·5	18	
1·073		640			+40·1	25·8	54	
1·070	1·070	205	350	84	+42·6	27·4	60	+0·29
1·066	1·066	632	380	91	−38	24·4	96	−0·35
1·064		720			−28·0	18·5	27	
1·059	1·059	215	260	60	−21	14	31	−0·25
1·059		603			+36·5	23·3	44	
1·054		641	(40)	(9)	+16·4	10·4	17	
1·049	1·049	613	340	78	−41·1	26	109	−0·40
							Average =	0·26

Complete data for all possible reflections to d= 1·05 Å are summarized in Table 2. The closeness with which a/c approximates the $\sqrt{2}$ leads to many incompletely resolved close doublets and multiplets, but in many cases diffractometer line profiles permitted graphical resolution of relative integrated counts for component members, and in such cases individuals are entered separately. Where this was not possible pairs are joined with braces. The overall average departure of $|I_o-I_c|/I_o$ is 0·26. To seek to improve this level of agreement (as by independent variation of Si–F distances) seems unjustified in a powder diagram.

The larger departures tend to occur for weak lines for which the amplitude contributions of the fluorine in the SiF_6 octahedra are large. For two extreme cases, in addition to this factor, resolution from a more intense near neighbor is difficult, and departures were paired to arrive at the 0·26 average. If unpaired it would be about 0·32.

A similar trend was noted by Hoard & Williams for $(NH_4)_3SiF_7$, and is presumably related to thermal activity of the SiF_6 octahedron as a unit, so that the individual thermal amplitudes are greater than those of independent ions in the same structure.

The placement of K_{II} is probably the best established feature. Although the diffraction lines were well beyond the range for reliable indexing, one substantial line at 0·889 Å and a moderate one at 0·938 have positions respectively corresponding to indices of 822 and 751 and of 820 and intensities which demand maximum contributions for K_{II}. These maxima are respectively at x=0·200 and x=0·208.

The structure is illustrated in Fig. 1 in basal projection and in a section parallel to (220). Various interatomic distances are summarized in Table 3.

Table 3. *Interatomic distances in* K_3SiF_7

$Si–F_{II,III}$	1·70 Å	(6)
$K_I–F_I$	2·78	(2)
$K_I–F_{II}$	2·92	(4)
$K_I–F_{III}$	3·34	(8)
$K_{II}–F_I$	2·78	(2)
$K_{II}–F_{II}$	2·83	(2)
$K_{II}–F_{III}$	2·58	(2)
	2·99	(4)
$F_{II,III}–F_{II,III}$	2·40	in octahedron
$F_{II}–F_{III}$	2·84	between octahedra
$F_{III}–F_{III}$	3·16	between octahedra

The 1·70 Å Si–F bond length in SiF_6 octahedra,

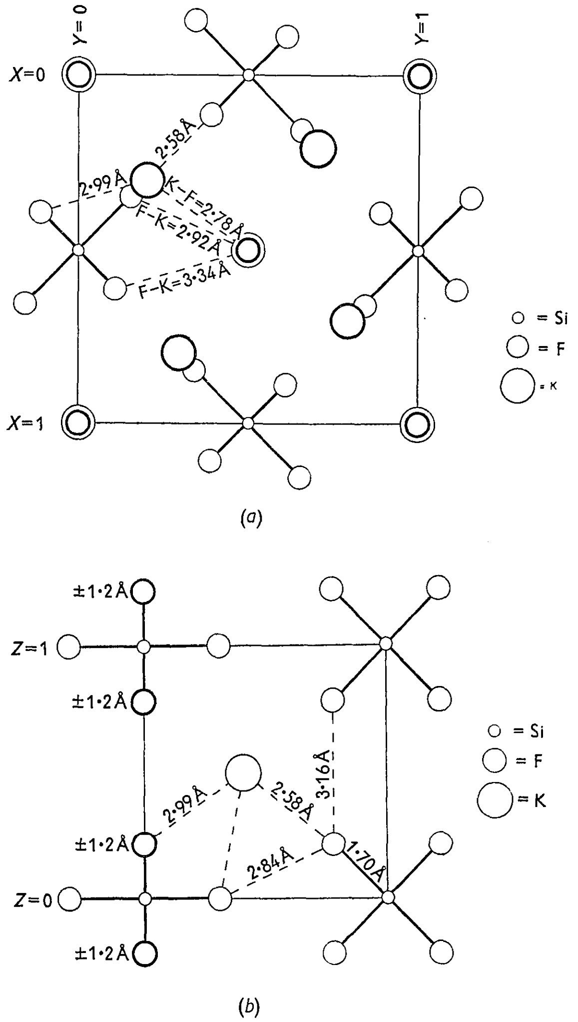

Fig. 1. The crystal structure of K_3SiF_7. (*a*) Basal projection. Heavy circles are at $z=\frac{1}{2}$. (*b*) A vertical section from $\frac{1}{2}$, 0 to 0, $\frac{1}{2}$. The basal projection is equivalent to that of Hoard & Williams as seen from beneath the plane.

arrived at on the assumption that all six bonds were equal, is probably valid to within some two or three hundredths of an Ångström. It is in agreement with the 1·71 Å determination by Hoard & Williams. Values as great as 1·8 Å, as reported for Na_2SiF_6 by Cipriani (1955), even if applied only to the Si–F_{II} distance, deteriorate agreement noticeably. Average departure for the 14 sensitive reflections above becomes 0·33.

The position of K_{II} in the polyhedron bounded by its 10 near neighbors is of interest. The polyhedron shares faces with each of two SiF_6 octahedra and corners with each of two others. The displacements from the triads comprising a silicon octahedron face are 2·99, 2·99 and 2·83 Å, but from the shared corner only 2·58 Å. K_I also shares faces with SiF_6 octahedra, and is displaced from those triads 3·34, 3·34 and 2·92 Å.

Reference to Hoard & Williams discloses that for their trial structure they took a central placement for NH_4 in its polyhedron, but their subsequent preferred parameters displace it 0·2 Å away from the shared faces toward the shared corners.

The structure as a whole consists of a relatively well coordinated tetragonal framework of composition K_2SiF_6 through which infinite channels parallel to *c* adduct strings of alternating K and F ions. K_I and F_I each have essentially the environments they assume in the potassium fluoride cube, but are somewhat further removed from analogous neighbors.

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