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The structure of $KAlSiO_4$ with $P6_3mc$ symmetry

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Abstract

Hexagonal $KAlSiO_4$ produced from nepheline by alkali exchange in molten KCl shows different diffraction effects from different crystals, even from the same exchanged batch. These crystals show variable degrees of diffuse streaking parallel to c^*, and the observed diffraction symmetries range from that of the kalsilite space group, $P6_3$, to that of space group $P6_3mc$. Study of the crystal structure of this latter symmetry phase reveals a kalsilite-like arrangement but with positionally disordered oxygen atoms. The disorder is attributed to a domain structure. Transformation of nepheline to kalsilite proceeds by tetrahedral rotation such that successive (00·1) layers undergo opposite-sense rotations. Where this sequence is interrupted, out-of-phase domain boundaries occur.

Introduction

As part of a study of Si–Al ordering in nepheline (Dollase and Peacor, 1971) Na-exchange nepheline, $NaAlSiO_4$, and hexagonal $KAlSiO_4$ were produced by a solid-state alkali exchange in molten chlorides. The compositions of the phase or phases produced depends upon the ratio of nepheline to alkali chloride. The procedure has been described by Wyart and Michel-Lévy (1955), Debron (1965), and others. The kinetics of unmixing in intermediate members of the nepheline–kalsilite series were recently studied by Yund *et al.* (1972), using similar preparative methods.

The crystal structure of kalsilite (near $KAlSiO_4$ composition) was reported by Perrotta and Smith (1965). That structure determination was made on a naturally occurring unmixed nepheline–kalsilite intergrowth, and demonstrated that the symmetry of kalsilite is hexagonal, $P6_3$. In a single-crystal X-ray examination of grains produced in the present study by K-exchange starting from nepheline, a kalsilite-like phase has been found. It was noted that many crystals of this phase show disorder diffuse streaking parallel to c^* with different crystals showing different degrees of streaking, and that the intensities of the *hhl*, *l*-odd reflections vary from crystal to crystal. Further examination showed that this class of reflections is in fact systematically absent in some crystals, which then exhibit over-all diffraction symmetry $6/mmm$ $P{*}{*}c$. A crystal-structure analysis of this phase was undertaken in order to determine its structural relationship to normal $P6_3$ kalsilite.

Alkali exchange procedure

Crushed samples of nepheline from Larvik, Norway (same sample as used in the crystal-structure refinement of nepheline, Dollase, 1970) were mixed with powdered KCl in various proportions and heated at temperatures near 800°C in crimped gold capsules for periods of 18 to 100 hours. The compositions of the resulting phase or phases were determined by X-ray powder diffraction measurements (Smith and Tuttle, 1957). Sample 9, which yielded crystal 9A used for intensity measurements, was prepared from a mixture of 5 parts by weight of KCl to 1 part nepheline, held at about 780°C for 24 hours. Using the variation in cell volume as a function of composition reported by Smith and Tuttle, crystal 9A has a composition of about $Ks_{96}Ne_{04}$.

Symmetry of alkali-exchanged kalsilite

In order to document the existence of all stages between crystals with *hhl*, *l*-odd reflections absent, to normal kalsilite with symmetry $P6_3$ (and therefore *hhl*, *l*-odd reflections clearly present), precession photographs were scanned with a microdensitometer measuring X-ray intensities along reciprocal lattice lines containing *hhl* and in particular 11*l*. Intensities from twelve single crystals, taken from 8 different exchanged batches, were measured and normalized to the same scale such that the sum of the 11*l*, *l*-even reflections was constant. Some crystals from the same exchange batch show markedly different *hhl* *l*-odd intensities, and there is no apparent correlation of these intensities with the slight differences in run durations, temperatures, or starting compositions. The normalized intensities of the 11*l*, *l*-odd reflections for the twelve different crystals are shown in Figure 1. A nearly continuous gradation exists from single crystals with *hhl*, *l*-odd (essentially) absent to those with strong *hhl*, *l*-odd reflections.

There are two differences between the hexagonal diffraction symmetries $P6_3$** and P**c, namely the presence or systematic absence of reflections of the type *hhl*, *l*-odd, and secondly the equality (in the case of P**c) or nonequality (in the case of $P6_3$**) of reflections *hkl* and *khl*, *i.e.* a difference in Laue groups 6/*m* or 6/*mmm*. This second difference, however, is not very diagnostic in this particular case, as the intensities of *hkl* and *khl* are also very nearly the same in normal $P6_3$ kalsilite. Perrotta and Smith (1965) apparently considered $P6_322$ (the uniquely determined space group if Laue group 6/*mmm* is accepted) to be a possible space group, but it was ultimately discarded in favor of $P6_3$ on the basis of agreement of observed and calculated structure factors. Finally, the effects of twinning on the diffraction pattern should be considered. Pervasive macroscopic twinning [*e.g.* with (11·0) twin plane] could account for an apparent 6/*mmm* diffraction symmetry, but the reflections of the type *hhl*, *l*-odd would then be expected to be present, being merely the sum of the intensities contributed by the various component subgrains.

Structure analysis

Crystal 9A, which shows no observable *hhl*, *l*-odd intensities above the streak background, was selected for X-ray intensity measurements. This crystal measured about 0.1 × 0.1 × 0.03 mm. Cell dimensions were measured on precession photographs, yielding values of a = 5.153(5) and c = 8.682(9) Å. These are similar to those of Perrotta and Smith of 5.161(4) and 8.693(5) Å. The intensities of 364 reflections were measured on a manual three-circle single-crystal diffractometer of the Weissenberg type using Zr-filtered Mo$K\alpha$ radiation. The data were corrected for absorption (μ = 17 cm^{-1}) using a polyhedral approximation, and for Lp factors.

Refinement of the structure was started using the positional parameters and symmetry $P6_3$ of Perrotta and Smith's kalsilite model. A difference Fourier map showed, however, that the O(2) site was only half occupied, with an additional half-oxygen electron density peak at a location mirror-equivalent to the O(2) atom, *i.e.* the O(2) atom is disordered between two sites. Because all atoms except O(2) are in special positions, disordering of O(2) to a mirror-equivalent site produces a structure of symmetry $P6_3mc$. Reflections of the type *hkl* and *khl* were compared and

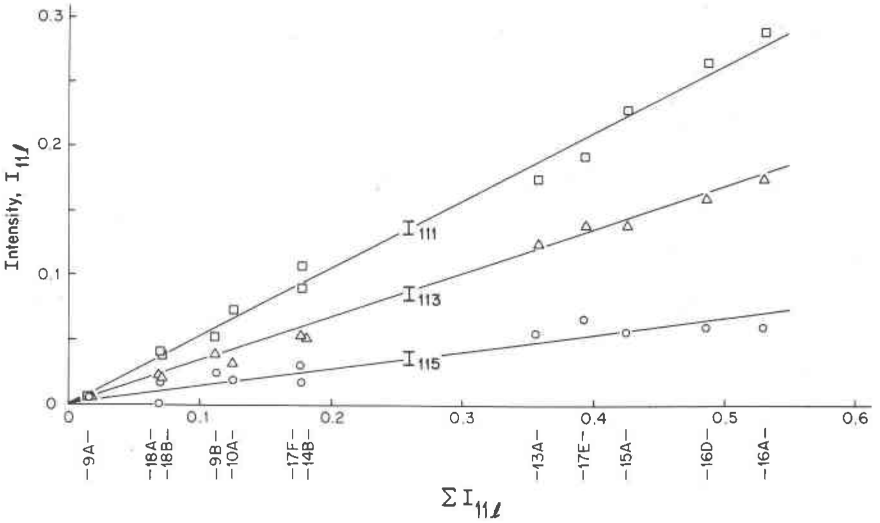

Fig. 1. Intensities of reflections of the type *hhl*, *l*-odd for various kalsilite single crystals. The intensities from the different crystals were scaled such that $\Sigma = (I_{112} + I_{114} + I_{116})$ is constant. The individual intensities (ordinate scale) and sum of odd-order intensities (abscissa scale) are given as fraction of Σ.

found to agree closely. Deviations averaged about 7 percent, with stronger reflections showing better agreement. Consequently the data were averaged to Laue group 6/*mmm*, resulting in 228 independent reflections. Refinement was then continued in space group *P*6$_3$*mc*. A second difference Fourier map showed the O(1) atom to be slightly displaced from the 3-fold axis (as is commonly found in these tridymite-like structures) from its position at 1/3 2/3 *z* to about 1/3 *y z*. Although the symmetry of the off-axis site does not require the *a*-axis coordinate to remain 1/3, this value was indicated in the Fourier map and retained in the subsequent refinement. The refinement converged at a final *R*-value of 9.8 percent for all reflections employing unit weighting. This rather high residual is probably due in part to the extensive disorder characterizing this material. Final refined positional and thermal parameters are given, along with those of Perrotta and Smith, in Table 1. Comparison of observed and calculated structure factors is given in Table 2.

Description of the structure

Although the structures of *P*6$_3$ and *P*6$_3$*mc* KAlSiO$_4$ are shown below to be different, the coordinates of their constituent atoms (each referred to its own space group) are the same within statistical uncertainty, as can be seen in Table 1. The small differences in thermal parameters are of uncertain significance.

The relationship between the phases is illustrated in the (00·1) projection shown in Figure 2. In this schematic drawing the structure in regions farthest from the line *AA'* is the ideal *P*6$_3$ kalsilite atomic arrangement. A unit cell is shown in dotted outline. This structure is composed of layers of 6-membered rings of SiO$_4$ and AlO$_4$ tetrahedra with large K-atoms (not shown) occupying positions at the centers of these rings. The Si-containing tetrahedra point toward the viewer, and the Al-containing tetrahedra point away. Note that the tetrahedra are rotated (around *c*) from a perfect hexagonal ring configuration to a ditrigonal ring configuration. In ideal kalsilite, within any one (00·1) layer all the ditrigonal rings "point" in the same direction (say along one of the *a* axes), whereas in the next layer they point in the opposite direction. The *c*-axis repeat is therefore two layers, and the rotation produces a staggering of tetrahedra, so that both layers may be discerned as in Figure 2.

The addition of a mirror plane normal to an *a*-axis produces the *P*6$_3$*mc* structure. Because of the short distance between the two mirror-equivalent O(2) sites, only one of these can be occupied at one time. Considering the strong Si–O or Al–O bonding that is present, it is reasonable that neighboring O(2) sites are occupied in such a manner as to maintain approximate tetrahedral geometry. The individual tetrahedra would thus have the same local configuration as in kalsilite, *i.e.* they are rotated (either CW or CCW) about the *c* axis. The disordered (*P*6$_3$*mc*) structure can be considered as the average structure

Table 1. Positional and thermal parameters of *P*6$_3$*mc* KAlSiO$_4$ compared to those of *P*6$_3$ kalsilite after Perrotta and Smith (second line entries).

	x	y	z	B	B(11)[e]	B(22)	B(33)	B(12)	B(13)	B(23)
K	0	0	.25[b]	1.67[f]	193(9)[a]	B(11)	45(4)	B(11)	0	0
	0	0	.25[c]	1.18(3)	148(5)		34(7)			
Si	1/3	2/3	.437(1)	0.64	63(14)	B(11)	35(18)	B(11)	0	0
	1/3	2/3	.437(1)	.35(4)	44(5)		18(8)			
Al	1/3	2/3	.056(1)	0.83	110(22)	B(11)	31(7)	B(11)	0	0
	1/3	2/3	.055(1)	.51(7)	63(9)		-5(14)			
0(1)[d]	1/3	.720(3)	.258(4)	.9(4)	-	-	-	-	-	-
	.334(3)	.716(2)	.259(4)	.9(3)						
0(2)	.614(2)	.019(3)	.993(3)	-	123(42)	12(33)	117(14)	2(61)	132(72)	109(43)
	.617(1)	.013(1)	.995(1)	1.01(5)	77(12)	84(11)	95(8)	39(8)	-20(17)	-16(11)

a. *standard deviations, in parentheses, in units of the final digit shown*
b. *to fix origin*
c. *0.0089 added to z-coordinates of Perrotta & Smith case B, so origins coincide*
d. *0(1) and 0(2) notation reversed from that of Perrotta & Smith*
e. *anisotropic temperature factors x* 10^4, *of the form* $\exp-(b_{11}h^2 + \ldots b_{12}hk + \ldots)$
f. *equivalent isotropic temperature factors - for 0(2) equivalent B indeterminate*

obtained by averaging over regions of the crystal where the tetrahedra are rotated at a CW fashion and over regions where the tetrahedra are rotated in a CCW fashion. A model of this composite crystal with both senses of rotation present can be seen in Figure 2. Note that at the lower left-hand corner the ditrigonal rings are oppositely oriented relative to those in the upper right-hand corner of the figure. The two opposing senses of rotation are produced, in this schematic illustration, by a structural "fault" centered along the line *AA'*. Away from this line the structure is locally ordered (into the ideal kalsilite arrangement), and thus the composite $P6_3mc$ crystal is proposed to consist of domains of kalsilite structure separated by domain boundaries at which the sense of tetrahedral rotation is reversed. The orientation of these small domains is related by the operation of a mirror plane perpendicular to *a*, producing an overall $P6_3mc$ symmetry. Although the domains may therefore be considered in a twin relationship, the sizes of the domains are evidently small enough that the structure factors combine vectorially (which, in the case of *hhl* reflections, means cancellation).

The actual boundary structure shown is only hypothesized. It is plausible in that it produces the requisite ditrigonal ring reversal with a minimal disturbance of the polyhedral connectivity. A similar reversal structure has in fact been found to occur in the structure of meteoritic low-tridymite (Dollase and Baur, 1976). Other domain boundary orientations and configurations are of course possible. In particular, a simple, low-energy domain boundary should occur parallel to (00·1). In this case the normal alternation of layers would be interrupted, producing two successive layers having the same sense of rotation, *i.e.* the 6-membered ditrigonal rings would superimpose in a (00·1) projection. The diffuse streaking along c^* observed in the diffraction patterns suggests that the normal two-layer periodicity along *c* is much more frequently interrupted than the periodicity of the structure perpendicular to *c*.

It seems probable that the disordering is a result of pseudosymmetry of the precursor nepheline structure. In nepheline the six-membered rings, although not ditrigonal, have a near-identical configuration in successive layers, giving rise to strong $P6_3/m$ pseudosymmetry (Dollase, 1970). Reorganization of the nepheline structure to kalsilite can be accomplished by simple rotation of the tetrahedra (all clockwise in one layer and all counterclockwise in the next layer) starting from the "neutral" nepheline configuration. For any one layer it is arbitrary whether its tetrahedra rotate in one sense or the other, although if the adjoining regions are already rotated it is likely that the rotation will be in the appropriate sense to continue the kalsilite arrangement.

During alkali exchange, nucleation of kalsilite-like regions probably occurs in many different locations within the crystal. As exchange proceeds, a domain would grow outward until it merged with another domain having the same tetrahedral rotation sequence, or until it encountered a domain with the

Table 2. Observed and calculated structure factors.

h	k	Fo	Fc
		ℓ = 0	
0	1	164	166
1	1	1169	1116
0	2	335	297
2	2	762	806
0	3	1175	1206
1	3	209	151
2	3	99	100
3	3	502	511
1	4	551	547
2	4	134	81
3	4	93	25
4	4	253	224
0	5	178	166
1	5	85	37
2	5	398	405
3	5	71	62
0	6	377	376
1	6	94	61
2	6	49	1
0	7	0	39
1	7	208	209
		ℓ = 1	
0	1	519	506
0	2	355	364
1	2	284	292
0	3	19	33
1	3	206	214
2	3	152	160
0	4	171	206
1	4	32	25
2	4	132	111
3	4	118	104
0	5	143	125
1	5	110	102
2	5	67	15
3	5	52	68
0	6	79	67
1	6	93	83
2	6	54	71
0	7	115	86
1	7	32	42
		ℓ = 2	
0	0	613	621
0	1	821	827
0	2	299	307
1	2	530	511
2	2	130	51
0	3	214	240
1	3	519	507
2	3	218	214
3	3	61	87
0	4	405	407
1	4	38	36
2	4	330	321
3	4	228	222
4	4	36	18
0	5	123	108
1	5	259	262
2	5	100	120
3	5	90	91
0	6	79	65
1	6	230	231
2	6	116	142
0	7	115	114
1	7	0	45
		ℓ = 3	
0	1	342	377
0	2	356	375
1	2	350	358
0	3	35	28
1	3	297	304
2	3	270	276
0	4	294	286
1	4	41	23
2	4	223	227
3	4	175	179
0	5	227	237
1	5	220	216
2	5	30	15
3	5	117	145
0	6	70	62
1	6	146	162
2	6	135	141
		ℓ = 4	
0	0	1179	1176
0	1	202	203
1	1	415	353
0	2	419	424
1	2	227	201
2	2	278	282
0	3	505	520
1	3	139	96
2	3	230	240
3	3	201	187
0	4	121	121
1	4	183	172
2	4	104	73
3	4	101	86
4	4	0	47
0	5	266	268
1	5	104	99
2	5	151	166
3	5	126	131
0	6	145	128
1	6	67	55
2	6	99	77
0	7	123	107
		ℓ = 5	
0	1	596	592
0	2	504	524
1	2	442	461
0	3	47	21
1	3	350	356
2	3	296	301
0	4	311	313
1	4	41	19
2	4	231	232
3	4	160	160
0	5	241	246
1	5	223	218
2	5	41	13
3	5	134	127
0	6	36	54
1	6	165	145
		ℓ = 6	
0	0	473	492
0	1	126	124
1	1	738	754
0	2	55	57
1	2	68	70
2	2	458	480
0	3	395	405
1	3	150	114
2	3	66	24
3	3	278	271
0	4	67	81
1	4	369	370
2	4	116	83
3	4	42	45
4	4	179	192
0	5	45	70
1	5	45	54
2	5	167	179
0	6	217	222
1	6	100	66
		ℓ = 7	
0	1	148	129
0	2	126	146
1	2	145	144
0	3	0	14
1	3	111	108
2	3	115	114
0	4	112	92
1	4	19	14
2	4	38	107
3	4	28	62
0	5	121	100
1	5	114	107
2	5	10	10
0	6	0	43
1	6	134	67
		ℓ = 8	
0	0	57	66
0	1	355	350
1	1	213	195
0	2	401	403
1	2	309	313
2	2	140	128
0	3	75	66
1	3	245	236
2	3	290	277
3	3	54	83
0	4	224	231
1	4	141	122
2	4	173	161
3	4	159	147
0	5	249	273
1	5	179	170
2	5	111	57
0	6	62	80
		ℓ = 9	
0	1	77	39
0	2	0	19
1	2	0	20
0	3	42	9
1	3	81	32
2	3	41	24
0	4	59	44
1	4	45	10
2	4	0	39
0	5	43	31
1	5	21	41
0	6	0	32
		ℓ = 10	
0	0	393	393
0	1	12	30
1	1	447	449
0	2	0	41
1	2	82	24
2	2	370	330
0	3	310	311
1	3	83	38
2	3	33	33
3	3	195	203
0	4	0	38
1	4	262	261
2	4	44	34
0	5	24	53
1	5	30	19
		ℓ = 11	
0	1	221	210
0	2	207	187
1	2	204	172
0	3	66	6
1	3	155	148
2	3	106	119
0	4	157	141
1	4	35	7
0	5	122	105
		ℓ = 12	
0	0	202	151
0	1	137	119
1	1	112	106
0	2	126	132
1	2	96	108
2	2	45	76
0	3	121	108
1	3	97	84
2	3	111	98
0	4	49	81
		ℓ = 13	
0	1	149	134
0	2	99	122
1	2	104	114
0	3	65	3
1	3	101	107
		ℓ = 14	
0	0	44	59
0	1	74	109
1	1	13	53
0	2	36	93

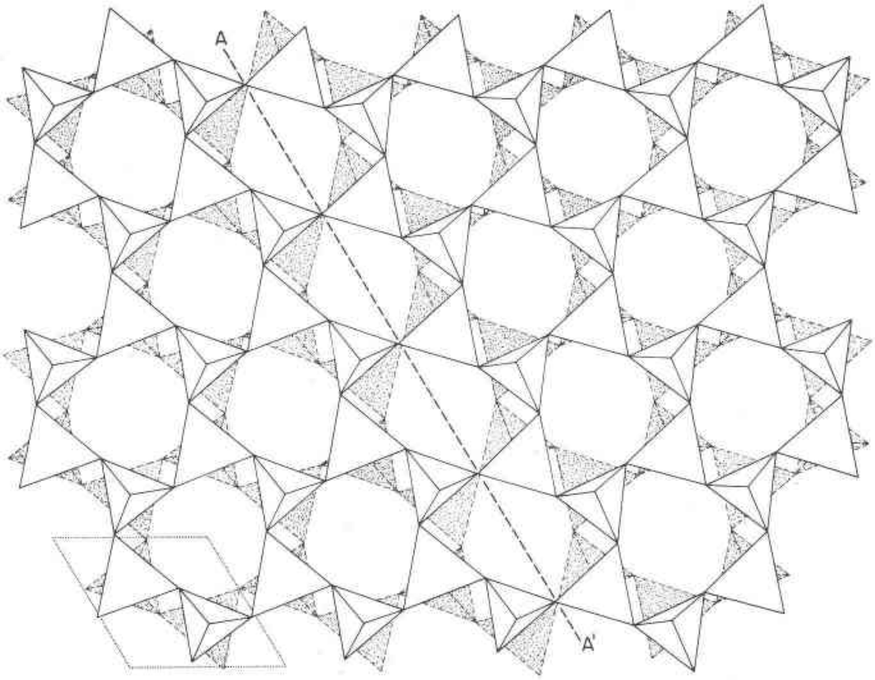

Fig. 2. (00·1) projection of a model of the $P6_3mc$ $KAlSiO_4$ structure.

opposite sequence, thereby forming an out-of-phase domain boundary.

Acknowledgments

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