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The renfinement of the structure of synthetic kalsilite

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Abstract

Several crystals of kalsilite were synthesized and the structural refinement was carried out to elucidate the structural detail of the pure end-member of the $KAlSiO_4$. The crystal is hexagonal, $P6_3$, with a=5,151(5) and c=8.690(8)Å. The structure was refined by the full-matrix least-squares method on the basis of counter measured intensity data. The structure agrees with those of the natural specimen. But it has the same domain structure as alkali-exchanged specimens investigated previously. The oxygen atoms which link tetrahedral atoms forming ditrigonal rings are disordered at two mirror-equivalent sites. The site occupancy ratio of oxygen atoms between these two positions were also refined on the assumption of the existence of domain structures inside the X-ray coherent regions. The final R-value is 0.084 for 373 observed reflections. While the alkali-exchanged specimens give diffuse streaks parallel to the c^* direction corresponding to the structural disorder in the stacking on the (001) plane, the specimens now investigated give sharp diffraction spots along the c^* direction. The ratio of the volumes of the coherent range of domain structure differs from one specimen to another. The structural relation between the two $P6_3$ domain structures corresponds to the twinning by merohedry after the classification by Friedel.

Introduction

Kalsilite, $KAlSiO_4$, is one of the important minerals in feldspathoids. Since Bannister and Hey (1942) described this mineral for the first time, the structure has been assumed to be those having tridymite-like frameworks with reference to the structure of $BaAl_2O_4$, $KLiSO_4$ and nepheline on the basis of the similarity of lattice dimensions and X-ray powder patterns (Claringbull and Bannister, 1948). Later, the accurate structure determination of nepheline was carried out by Buerger, Klein and Donnay (1954).

Smith and Sahama (1957) carefully studied a kalsilite by means of single crystal X-ray method, and observed diffuse reflections in addition to strong, sharp ones. They concluded that the diffuse reflections were caused by the ordering of the tetrahedral atoms and suggested the occurrence of the two types of kalsilite: o-kalsilite (ordered form, a=8.9 Å) and d-kalsilite (disordered form, a=5.15 Å). The o-kalsilite has super-

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cells taking the positions rotated by 30° to the d-kalsilite cell around the *c*-axis.

An accurate structural refinement of kalsilite was performed by Perrota and Smith (1965), who proved that the structure of kalsilite was derived from that of tridymite by rotating the tetrahedra in the (001) plane. This refinement confirmed that the silicon and aluminum atoms are ordered because the tetrahedral distances (T–O) are 1.61 and 1.74 Å, respectively. Therefore, the space group of kalsilite was strictly determined as $P6_3$. Oxygen atoms connecting Si-Al tetrahedra occupy statistically threefold positions displaced by 0.25 Å from the ideal positions on triad axes, and the bond angles decrease to 163°.

Recently Dollase and Freeborn (1977) produced kalsilite from nepheline by alkali exchange in molten KCl. They carefully examined the diffraction symmetry, the intensity distribution and the existence of diffuse scattering by means of Weissenberg and precession methods. As a result of these experiments, they observed that the intensities of the reflections of the type *hhl*, with *l*-odd were different from a crystal to another. Among the many specimens obtained in the experiment, they found one crystal, in which no *hhl*, with *l*-odd reflections were observed. The structure refinement was carried out on this specimen using counter-measured intensity data. The refinement gave not only the same structure as natural kalsilite reported by Perrota and Smith (1965), with ordered tetrahedral Si-Al atoms and displaced oxygen atoms from ideal tridymite-like framework structures, but also having arrangements which are the same as other positionally disordered oxygen atoms which link tetrahedral atoms in the (001) plane. Dollase and Freeborn (1977) concluded that these apparent positions of O atoms might be attributed to a domain structure, whose volumes were small enough to diffract X-rays coherently, in which the oxygen atoms connecting tetrahedral atoms were displaced from positions having $P6_3$ symmetries into mirror equivalent positions in accordance with the symmetries of $P6_3mc$.

Under these circumstances, the authors thought that it would be important to study the condition of the formation of the domain structure and also refine the structure of synthetic pure end-member of kalsilite. For this purpose, kalsilite crystals were synthesized by hydrothermal method and the crystal structure having the masses with certain domain ratio was refined by full-matrix least squares program modified for site occupancy refinement calculations, using three-dimensional counter-measured intensity data.

Experimental

The synthesis of kalsilite was tried by both dry and hydrothermal methods. Starting materials consist of a reagent mixture of SiO_2, Al_2O_3 and K_2CO_3. K_2CO_3 was added in excess of the stoichiometric amount, and a few starting materials contain both K_2CO_3 and Na_2CO_3. Kalsilite was obtained on the synthesis by hydrothermal method with the test-tube type apparatus. The synthesis by dry method produced synthetic kaliophilite, another polymorph of $KAlSiO_4$ (Smith and Tuttle, 1957). Kalsilite crystals were obtained at about 600°C, 1000kg/cm^2 within 15 days. They were colorless with euhedral forms. The crystal habit varies with the degree of the excess of K_2CO_3 in the starting materials: platy, granular and needle-like.

Kalsilite was also synthesized from starting materials containing Na_2CO_3 which takes the place of K_2CO_3, where the K_2CO_3 content is still excess enough to produce $KAlSiO_4$. The measured cell-dimensions of the obtained crystals, however, indicates that the product is kalsilite containing potassium alone as alkali atoms. This suggests that potassium atoms occupy the alkali sites more easily than sodium atoms, and supports the site preference explained by Dollase and Thomas (1978).

The approximate cell dimensions and the intensity distribution were estimated from Weissenberg and precession photographs taken with CuKα radiation (λ=1.5418Å). The diffraction symmetry obtained was $P6_3$–with *hhl, l*-odd present. The specimens examined in this study gave sharp diffraction spots parallel to the c^* direction, and the diffuse streaks along the c^* direction were not observed in the photographs. Thus the space group derived from diffraction symmetry and extinction rules was consistent with $P6_3$ or $P6_322$.

The crystal, which was selected for X-ray intensity measurements, is the hexagonal prism elongated along the c-axis and with approximate dimensions 0.2x0.2x0.6mm. Three-dimensional intensities were collected on an automated four-circle diffractometer using the 2θ-ω scan technique, and MoKα radiation (λ=0.70926 Å) with graphite monochromator. 504 intensities were collected up to 2θ=86°, of these 373 with $I>3\sigma$ above background were classified as observed. The intensities were converted to the structure factors by applying the Lorentz-polarization correction. Absorption corrections were not carried out. Accurate cell dimensions were calculated by least-squares methods using 20 values of 25 diffraction peaks measured by the same diffractometer. The crystal data, such as cell dimensions and their standard deviations are listed in Table 1. The values of cell dimensions are close to the previously reported ones. The powder diffraction data collected are also given in Table 2.

TABLE 1. Crystal data of synthetic kalsilite.

Chemical formula	$KAlSiO_4$ with Z=2
Space group	$P6_3$
Cell dimensions	a=5.151(5) Å
	c=8.690(8) Å
Density	D_X=2.635 Mg/m^3

TABLE 2. The X-ray powder data of synthetic kalsilite.

d (obs.)	*I* (obs.)	*hkl*	*d* (calc.)
4.363 A	23	002	4.345
3.985	54	101	3.969
3.116	100	102	3.113
2.584	50	110	2.576
2.477	12	111	2.469
2.437	10	103	2.429
2.236	4	200	2.231
2.223	10	112	2.216
2.177	20	004	2.172
2.166	6	201	2.161
1.990	5	202	1.984
1.958	3	104	1.953
1.929	4	113	1.925
1.771	3	203	1.767
1.665	4	114	1.661
1.660	5	211	1.655
1.623	7	105	1.619
1.575	7	212	1.572
1.551	2	204	1.556
1.490	8	300	1.487

Structure refinement.

Five cycles of full-matrix least-squares calculation were repeated with the space group $P6_3$, starting from the positional parameters of the natural kalsilite published by Perrota and Smith (1965). The values of atomic parameters and isotropic temperature factors were approximately converged to those of the natural kalsilite or the alkali-exchange kalsilite. However, R-value was not reduced to less than 0.119. A difference Fourier map showed that the O(1) atoms are disordered partly between two mirror-equivalent sites. These mirror planes are parallel to the longer diagonal of the unit cell corresponding to the $P6_3mc$ symmetries. Therefore, the multiplicities between O(1) and its mirror-equivalent oxygen were refined together with other parameters, using the full-matrix least squares program modified by the present authors for the site occupancy refinement, and the structure was converged to give the final R value of 0.084 for anisotropic temperature factors on the application of equal weights to all reflections. The rather high residual value may be due to the extensive positional disorder of O(1) atoms.

Scattering factors corresponding to neutral atoms were used for the structure factor calculations (International Tables for X-ray Crystallography, 1974).

Final positional parameters and equivalent temperature factors are shown in Table 3, and interatomic distances and angles are listed in Table 4.

TABLE 3. Positional and equivalent isotropic temperature factors of synthetic kalsilite with standard deviations in parentheses.

	X	Y	Z	$B_{eq.}$
K	0	0	0.25	1.25(5)
Al	1/3	2/3	0.054(2)	0.74(12)
Si	1/3	2/3	0.436(1)	0.45(9)
O(1)	0.610(2)	0.005(2)	0.993(2)	1.4(2)
O(2)	0.350(8)	0.713(4)	0.252(6)	1.0(3)

TABLE 4. Interatomic distances and angles of synthetic kalsilite.

Si–O(1)	1.65(1) Å	O(1)–Si–O(1)	111.2°
Si–O(2)	1.60(5)	O(1)–Si–O(2)	100.2°
mean Si–O	1.64		110.0°
			112.6°
			mean 107.6°
Al–O(1)	1.69(1)	O(1)–Al–O(1)	110.9°
Al–O(2)	1.73(5)	O(1)–Al–O(2)	101.9°
mean Al–O	1.70		114.0°
			107.9°
			mean 107.9°
K–O(1)	2.92(2)		
K–O(1)'	3.00(2)		
K–O(2)	2.84(4)		
mean K–O	2.92		

Description of the structure and discussions

Fig. 1 shows the (001) projection of the structure of synthetic kalsilite. The silicon and aluminum atoms are tetrahedrally coordinated by oxygen atoms. Each tetrahedron is connected by three O(1) atoms in the plane perpendicular to the *c*-axis and by one O(2) atom in the direction along the *c*-axis so they construct tridymite-like frameworks. This structure is almost the same as natural kalsilite but O(1) atoms are partly disordered between two sites, which are related each other by mirror planes

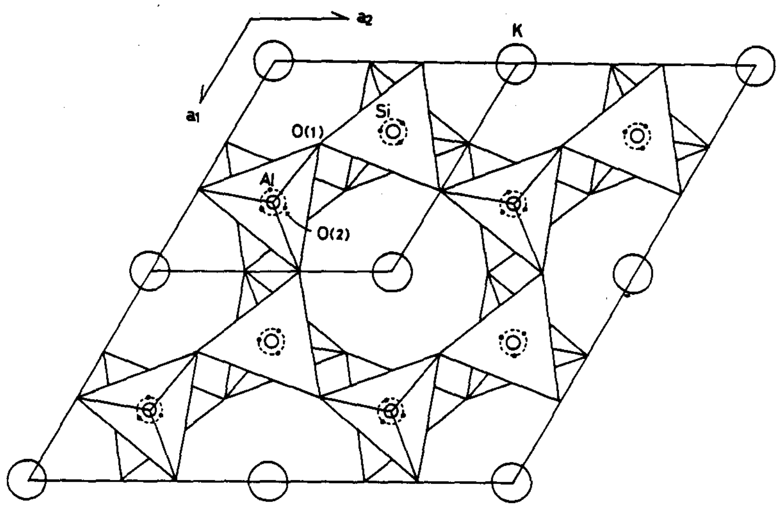

FIG. 1. The (001) projection of the structure of synthetic kalsilite. Each tetrahdron is connected by three O(1) atoms in the plane perpendicular to the c-axis and by one O(2) atoms in the direction parallel to the c-axis. O(2) atoms are distributed into three different positions near triad axis as shown by the dotted line in the figure.

perpendicular to the a-axis, O(2) atoms are statistically distributed over three sites displaced from the ideal positions, and the bond angle (T–O–T) is smaller than 180°. This signifies that the structure of synthetic kalsilite investigated here is the same as natural kalsilite structure determined by Perrota & Smith (1965) and, in addition, it has the domain structure, as revealed in the alkali-exchanged kalsilite (Dollase and Freeborn, 1977).

Fig. 2 shows the framework structure of silicon-aluminum tetrahedra of kalsilite. The structure contains the frameworks in two orientations (a) and (b) related each other by mirror planes through longer diagonals of the unit cell, or normal to the a-axis. The geometrical relation of this domain structure is compared to the case of twinning, where the twinned lattice coincides with the original lattice. This is the case of twinning by merohedry in the classification of twins after Friedel (1926). Since the R-factor was reduced to 0.084 after the site occupancy refinement between these mirror equivalent positions, it is supposed that these two domains interfere X-rays coherently, and the structure factors calculated for these two domains must be added vectorially. On the basis of this fact, the values of the structure factors in the various ratios of domain volumes were calculated. Fig. 3 shows the relation between the variation of the calculated structure factors of the type hhl, l-odd with the continuous change of the ratio of the domain volume ((a) and (b) type) and the values of F_{ob} measured for three different crystals. The values of the structure factors have been

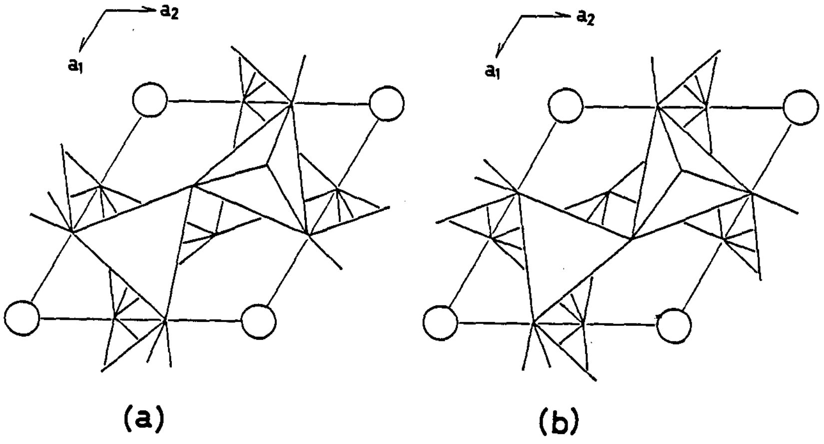

FIG. 2. Schema of the positional relationship of the domain structure. The structure has two types, (a) and (b), and these are related by mirror planes through longer diagonal of the unit cell.

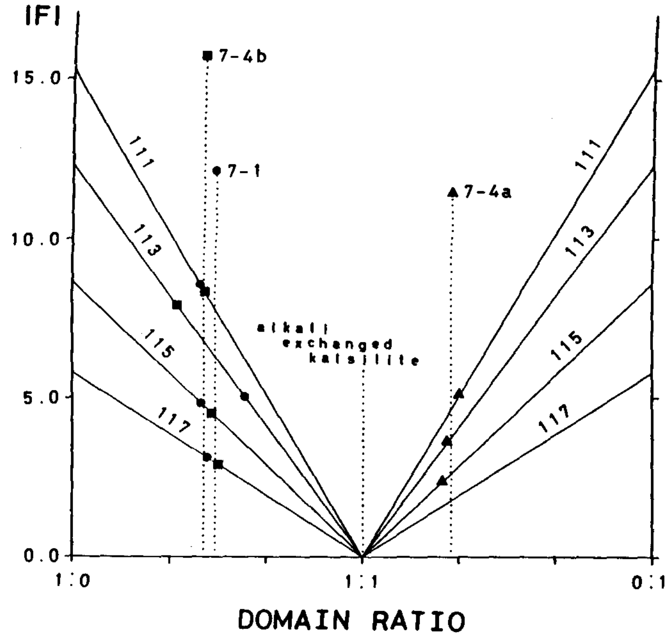

FIG. 3. A diagram showing the variation of the calculated structure factors of the type *hhl*, *l*-odd with the continuous change of the ratio of the domain volume (a) and (b) type. The observed structure factors of the three specimens, 7-1, 7-4a and 7-4b are plotted on the diagram. The straight lines correspond to the change of the values of the calculated structure factors 111, 113, 115 and 117. The vertical dotted lines are drawn on the mean values of the assumed domain ratio of the each specimen.

normalized to the same scale so that the sum of the values of the type *hhl, l*-even, which is constant for the change of the domain ratio, becomes constant for all the different crystals. The lines in the figure, however, are symmetrical at the center. Therefore, it is impossible to distinguish the domain ratio *m*:*n* from *n*:*m* only by the inspection of the structure factors of the type *hhl*. But it is possible to distinguished these two domain ratios with the aid of the structure factors of the type *hkl* and *khl* which are different for them. F_{ob} values of three different crystals are plotted in the figure. It is noted that different crystals have different domain ratios. This fact is in accordance with the result obtained by Dollase and Freeborn (1977), who interpreted that the domain structure is formed through the transformation from nephelines to kalsilite by the rotation of tetrahedra such that successive (001) layers undergo opposite-sense rotation. However, it is not reasonable that this interpretation is applied to the kalsilite synthesized by hydrothermal methods, because synthetic kalsilite does not have any diffuse streaks parallel to the c^*, while the alkali-exchanged specimen shows these streaks. It is possible to interpret this fact as follows. Since the alkali-exchanged kalsilite is produced from nepheline without breaking the tridymite-like framework, the domain boundaries can occur at the plane normal to the *c*-axis more easily than at the plane parallel to the *c*-axis. It is possible that the domain thickness along the *c*-axis is $n \cdot c/2$ (*n* is integers), which would cause the diffuse streaks. On the other hand, because the synthetic kalsilite is produced from non-crystalline materials, the domain boundaries could occur on the planes parallel to the *c*-axis as often as on the plane normal to the *c*-axis, probably the latter is less frequent. This fact probably explains the reason why the synthetic specimen does not have any diffuse streak parallel to the c^* in spite of the fact that the both specimen have the same domain structure.

The interatomic distances and angles are listed in Table 4. The values of Si–O (1.65, 1.60 Å), Al–O (1.69, 1.73 Å) agree with mean values of typical framework structures (Si–O:1.61; Al–0:1.75 Å),. A slightly larger value for Si–O and a smaller value for Al–O might show the partial disorder of Si and Al. The K–O distances of 2.92, 3.00 and 2.84 Å are consistent with those obtained by the previous investigators (Perrota and Smith, 1965; Dollase and Freeborn, 1977). The electrostatic valence sum calculated according to the method of Brown and Shannon (1973) is 3.70 for Si. 3.24 for Al, and 0.969 for K, corresponding to some degree of disordering in Si and Al sites.

Thus the synthetic and alkali-exchanged kalsilite exhibit very similar character, though the domain structure might be caused by different mechanisms.

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