Structural Modification of KAlSiO$_4$ Minerals

Yasuhiko OKAMOTO

The board of education of Okayama Prefecture
Uchisange 2–4–6, Okayama 700-8570, Japan

Kalsilite, a polymorph of KAlSiO$_4$ is an end member of nepheline–kalsilite series and the mineral was synthesized by hydorthermal methods. The synthetic kalsilite is hexagonal, $P6_3$, with $a = 5.151(5)$, $c = 8.690(8)$ Å. The structure was refined by full-matrix least-squares methods to a R-value 0.084, using 373 observed reflections. The obtained structure agrees well with those of the natural and the alkali-exchanged specimens reported in the previous literatures. The oxygen atoms are disordered at two mirror-equivalent sites, constructing the domain structure. The average domain structure shows $P6_3mc$ symmetry and the structural relation between the two $P6_3$ structure corresponds to the twinning by merohedry.

The domain structure was considered to be caused accompanied with the high–low inversion of the kalslite structure. Heating experiments of kalsilite reveal that the X-ray powder pattern changes at 865°C, and that cell dimensions vary discontinuously at this temperature. It was confirmed that kalsilite underwent a displacive transition like those observed in quartz or tridymite. The high-form is refered as 'high-kalsilite', and a possible simulate model is proposed.

The structure of the high-kalsilite at 950°C was refined byfull-matrix least-squares methods to a R-value 0.095, using 115 observed reflections. The high-kalsilite is also hexagonal, $P6_3mc$ or $P6_3/mmc$, with $a = 5.288(1)$, $c = 8.628(5)$ Å at 950°C. The structure almost prefectly coincides with that of the simulated model. Based on the interatomic distances, the distribution of silicon and aluminum atoms is found to be ordered and the space group is determined to be $P6_3mc$.

Kaliophilite and the related orthorhombic form, polymorphs of KAlSiO$_4$, were synthesized by dry method. The synthetic kaliophilite (kaliophilite-H2) is hexagonal with $a = 5.17(1)$, $c = 8.49(3)$ Å, and the orthorhombic KAlSiO$_4$ (kaliophilite-O1) is orthorhombic with $a = 9.01(1)$, $b = 15.60(2)$, $c = 8.53(4)$ Å. Detailed examination of the obtained powder patterns together with that of simulated model indicates that the kaliophilite-H2 has a disordered structure of four types of the low-kalsilite. The structure was refined by the X-ray powder pattern-fitting method (Rietvelt method) to a R-value 0.121.

Keywords: kalsilite, kaliophilite, feldspathoid, systheses, crystal structure

1 Introduction

Minerals of feldspar group are the most abundant constituents of igneous rocks and the most important minerals in the lithosphere. The minerals show wide range in chemical composition and the structures of the minerals is full of variety depending on the formation condition such as temperature and pressure together with the nature of the related magma (e.g. Ribbe, 1984).

Feldspathoid is aluminosilicates of mainly K, Na, or Ca, so it is similar to feldspar. Feldspathoid is characterized by unique composition with less silica than that of the corresponding feldspar. Minerals of feldspathoid group are important constituents of alkaline rocks deficient in silica. Among the feldspathoid group, minerals belonging to the nepheline (NaAlSiO$_4$: Ne) – kalsilite (KAlSiO$_4$: Ks) series are the most common in the nature. The investigation on the Ne–Ks series is very important for clarifying the crystallization mechanism of alkaline rocks.

The structures of the feldspathoid group have a framework of linked $(Si,Al)O_4$ tetrahedra. The structures of nepheline and kalsilite consists of the tridymite-like framework whose tetrahedral sites are occupied by aluminum and silicon atoms one after the other. The excess minus charges are compensated by Na^+ or K^+ ions in the cavities of the frameworks constructing six-memebered rings in the structure. In nepheline, the cavities of the structure are distorted one after the other from that of kalsilite. The detailed structures of these minerals are rather complicated, and vary according to chemical composition and/or thermal history. However, the structure of kalsilite can be well understood based on the wide comprehensive structural view point including the structure of nepheline. In this paper, detailed structure of kalsilite in the system of the Ne–Ks series will be examined.

Furthermore, many modifications are known in the Ne–Ks series. Numerous investigations on the two component system of the Ne–Ks series have been accumulated since 1940's. Among those, the phase relations of this system has been investigated in detail by Smith and Tuttle (1958), who established the phase equilibrium at sub-solidus temperatures between $NaAlSiO_4$ and $KAlSiO_4$ components. The two component system has the miscibility gap below approximately $1,000°C$ and the case is similar to that of the system $NaAlSi_3O_8$(albite)–$KAlSi_3O_8$(orthoclase). In the course of these investigations, Smith and Tuttle (1957) identified the following phases by X-ray powder methods and gave their X-ray data: high- and low-carnegieite, high- and low-nepheline, kalsilite, orthorhombic $KAlSiO_4$(O1), second orthorhombic phase(O2), natural kaliophilite, anomalous natural kaliophilite, synthetic kaliophilite and tetrakalsilite(H4). Further, Sahama and Smith (1957) described trikalsilite, and Cook, Roth, Parker and Negas (1977) synthe-

sized higher-temperature orthorhombic $KAlSiO_4$ obtained through the transition of O1-phase by heating.

In this report, the structures of the Ne–Ks series, especially $KAlSiO_4$ minerals (kalsilite and kaliophilite) will be investigated. Special attention will be paid on the following four points.

1. Syntheses of kalsilite by hydrothermal method, especially syntheses of single crystals fitted for the structural analyses.

2. The structural refinement of synthetic kalsilite and the comparison of the structure with that of natural kalsilite and the synthesized kalsilite by alkali exchange methods.

3. Measurement of the high–low inversion point of kalsilite and the structural refinement of high temperature form of kalsilite.

4. The structual refinement of synthetic kaliophilite and the comparison of the structure with that of kalsilite.

The general overview of the structures of feldspathoid minerals will be described in the next section and the research histories of the minerals will be mentioned at the beginning of each chapter.

1.1   Feldspathoid groups

The crystal structures of feldspathoid groups are characterized by three demensional framework, in which tetrahedra of $(Si,Al)O_4$ are linked to one another in all directions by shared oxygens. Feldspathoids are divided into three groups: leucite group, sodalite–cancrinite group and nepheline–kalsilite group (Merlino,1984).

In addition to the three groups Melilite, $(Ca,Na)_2(Mg,Fe,Al,Si)_3O_7$, is generally included in feldspathoid but the structure belongs to orthosilicate (Smith, 1953).

The structures of the three groups will be in the next briefly summarized. In each subsection, space groups and cell dimensions of the feldspathoid minerals are quoted from those of Merlino (1983).

1.1.1 Leucite group

The framework of the leucite group is intricate, but the framework can be best expressed in terms of a basic topology shown in Fig. 1-1(Merlino, 1984). The basic structure is formed by four-membered rings with $\bar{4}$ symmetry. Two four-membered rings and two tetrahedra located on opposite edges are linked, and construct ten-membered ring (Fig. 1-1 : a and b). The ten-membered ring constitutes a structural unit. These units are connected with each other forming three-dimensional networks (Fig. 1-1 : c). In the framework two kinds of cavity sites are present, which are occupied by cations or water molecules. The cavity sites occupied by cations are called S sites and those occupied by water molecules are called W sites (Fig. 1-1 : d). In the leucite-type structure cations occupy only W sites and/or both W and S sites, whereas in the analcime-type sturucture cations occupy only S sites and water molecules occupy W sites.

Leucite-type structures

Leucite, $K_{16}Al_{16}Si_{32}O_{96}$. is tetragonal ($I4_1/a$, $a = 13.04$, $c = 13.85$ Å) at the room temperature but inverts to cubic ($Ia3d$, $a = 13.43$ Å) at about 600°C. In the both structures, no Al–Si ordering is present and K^+ ions locate in W sites leaving S sites vacant. At the room temeperature K^+ ions are too small to fill the large W sites, and the resultant collapse of the framework yields the lower symmetry.

Pollucite, $Cs_{12}Na_4(Al_{16}Si_{32}O_{96})\cdot 4H_2O$, is a cesium replaced analog of leucite. In contrast with leucite, the symmetry of pollucite is cubic ($Ia3d$, $a = 13.69$ Å) even at the room temperature. In pollucite, twelve Cs^+ ions and four H_2O molecules are located in W sites, whereas four Na^+ ions located in S sites.

Analcime-type structures

The structure of analcime, $Na_{16}(Al_{16}Si_{32}O_{96})\cdot 16H_2O$, contains sixteen H_2O molecules in W sites and sixteen Na^+ ions in S sites. If there is no Al–Si ordering like in the cases of leucite and pollucite, the average symmetry of analcime is $Ia3d$. But the true symmetry is lowered to $I4_1/acd$, $a = c = 13.78$ Å because of Al–Si ordering in part.

The structure of wairakite, $Ca_8(Al_{16}Si_{32}O_{96})\cdot 16H_2O$, contains sixteen H_2O molecules in W sites and eight Ca^{2+} ions in S sites. Wairakite is considered to be the most ordered form of the analcime-type structures. Ordering of tetrahedra cations in analcime and wairakite is shown in Fig. 1-2 (Merlino, 1984). In the wairakaite structure perfect Al–Si ordering reduces the symmetry to $I4_1/acd$. Furthermore, Ca^{2+} ions in S sites cause distortion in the framework, and the true symmetry is lowered to $I2/a$, $a = 13.69$, $b = 13.68$, $c = 13.56$ Å, $\beta = 90.5°$.

1.1.2 Sodalite–cancrinite group

The basic crystal structure of sodalite–cancrinite group consists of six-membered rings linked to give three-dimensional networks, in which each ring is connected to three six-membered rings and these three rings are connected to other three rings and so on. The manner of ring connection is comparable to the stacking of spheres (ABCABC··· or ABABAB···).
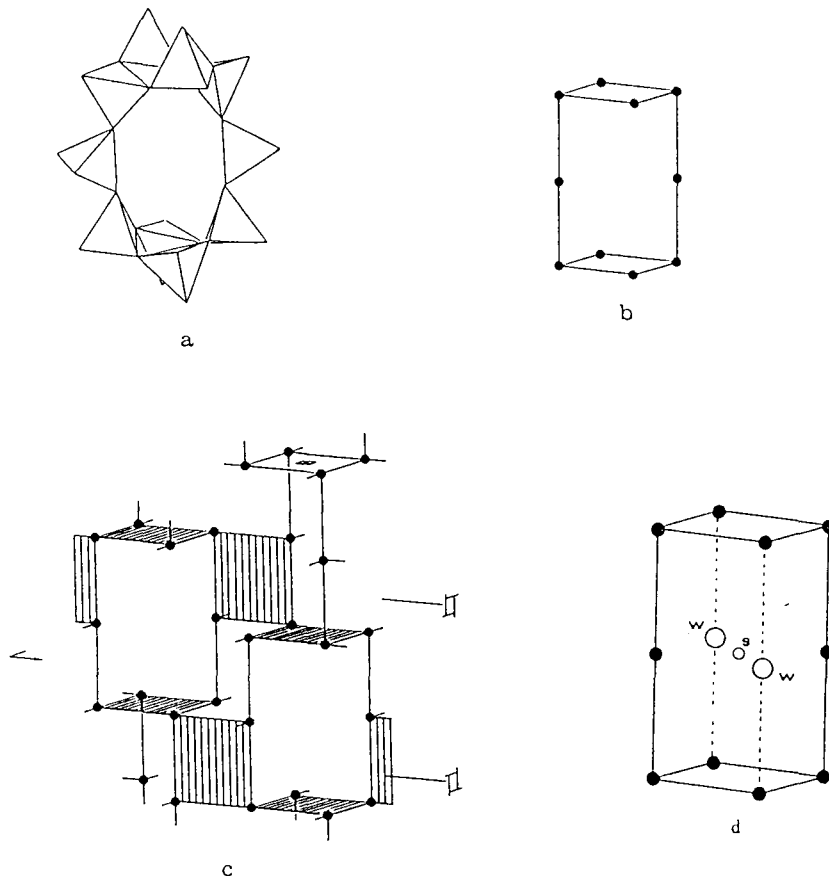
Fig.1–1: Schematic illustration of leucite structure (Merlino, 1984).

(a) ; prismatic cage, representing part of the leucite structure.

(b) ; simplified representation showing only the tetrahedral nodes and their connectivity.

(c) ; the connection between two adjacent columns of prismatic cages.
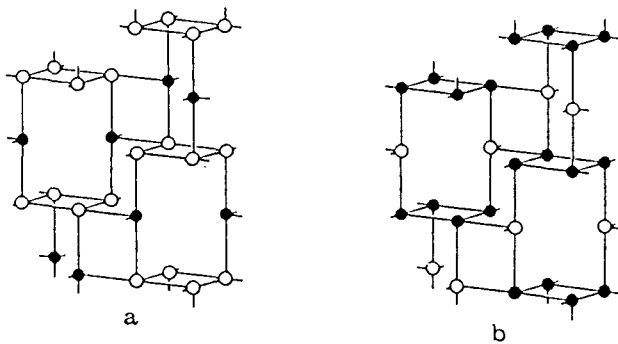
(d) ; S and W sites in the prismatic cage.

Fig.1–2: Ordering of tetrahedra cations in analcime
and wairakite (Merlino, 1984).

(a) ; Si, Al ordering in the basic structure of analcime.
Filled circles indicate silicon cations;
silicon and aluminum orderly alternate in
the four sites represented by open circles
and forming four-membered rings.

(b) ; Si,Al ordering in wairakite: filled and open
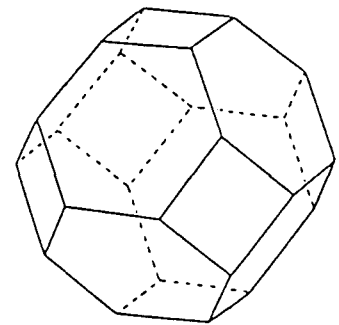circles indicate Si and Al respectively.

Fig.1–3: Truncated octahedral cage in
the sodalite-type structures
(Merlino, 1984).

Sodalite-type structures

In the framework of the sodalite-type structures, six-membered rings are connected with the manner of an ordered ABCABC$\cdots$ sequence. Therefore the symmetry of the sodalite-type structures is cubic. The framework can also be described with truncated octahedral connection of terahedral sites shown in Fig. 1 3(Merlino, 1984). The framework can be distorted to more extent so as to adapt the size for certain another ion in the cavity.

Sodalite, Na$_8$(Al$_6$Si$_6$O$_{24}$)Cl$_2$, is the most sodium-rich member in this family, and the space group is $P\bar{4}3n$ (a = 8.870 Å). In sodalite, (Na$_4$Cl)$^{3-}$ tetrahedral groups are located in each cavity with Cl$^-$ ions at 0, 0, 0 and 1/2, 1/2, 1/2. The eight hexagonal rings are tightened around these anions. Each Na$^+$ ion is linked to three oxygen atoms in the cavity.

Nosean has the composition of Na$_8$(Al$_6$Si$_6$O$_{24}$)SO$_4$. In the crystal structure of nosean, two Cl$^-$ ions of sodalite structure are replaced randomly by one (SO$_4$)$^{2-}$ ion per the cell of sodalite. The space goup of nosean is $P\bar{4}3m$ (a = 9.05 Å).

Haüyne, Na$_5$Ca$_2$(Al$_6$Si$_6$O$_{24}$)(SO$_4$)$_{1.5}$, differs chemically from nosean in containing a greater number of (SO$_4$)$^{2-}$ ions and has some Ca^{2+} ions replacing Na$^+$ ions. The space group of haüyne is $P\bar{4}3n$ (a = 9.116 Å).

Bicchulite, Ca$_8$(Al$_8$Si$_4$O$_{24}$)(OH)$_8$, is one of the most calcium-rich member in this family, and the space group is $I\bar{4}3m$ (a = 8.825 Å). In the crystal structure of bicchulite, the cavities are occupied by clusters with composition of Ca$_4$O$_{12}$(OH)$_4$ and each cluster consists of four CaO$_3$(OH)$_3$ octahedra. Twelve oxygen atoms are shared by four hexagonal rings in the framework.

Cancrinite-type structures

The crystal structure of cancrinite, Na$_8$(Al$_6$Si$_6$O$_{24}$)(CO$_3$)$_2$·5H$_2$O, is composed of simplest frameworks by connecting six-membered rings with the manner of ABABAB$\cdots$. The symmetry of cancrinite is hexagonal ($P6_3$, a = 12.75, c = 5.14 Å).

The crystal structure of microsommite, K$_9$Na$_{15}$(Al$_{18}$Si$_{18}$O$_{72}$)(CO$_3$)$_2$(SO$_4$)$_2$·7~8H$_2$O, hexagonal, a = 22.138, c = 5.248 Å, is the same to that of cancrinite except superstructures caused by horizontal ordering. Therefore, c is quite similar to that of cancrinite, but a is $\sqrt{3}$ times of that of cancrinite.

1.1.3 Nepheline–kalsilite group

In this group, the basic structure of each phase has defferent topology in contrust with two groups mentioned above. These phases are the main topics of this report, and will be discussed in detail in the following sections.

1.2 Nepheline

Nepheline, one of the representative minerals in nepheline–kalsilite group, possesses hexagonal symmetry, and can be expressed simply by the formula NaAlSiO$_4$. However, almost all natural nephelines contain potassium, more silicon and less aluminum than those indicated by the formula. Moreover, the substitution of calcium and ferric ions is possible(Bannister, 1931 ; Tilley, 1954).

Bannister (1931) revealed that the content of the unit cell is (Na,K,1/2Ca)$_x$Al$_x$Si$_{16-x}$O$_{32}$ (x = 6.6 to 8.2) based on the chemical analysis, and suggested that an approximate structure is basically composed of tridymite-type structure, i.e., a derivative of the high-tridymite structure(Buerger, 1954). The proposed structure reasonably explains variable composition of natural nephelines,

Buerger, Klein and Donnay (1954) first determined the approximate structure of nepheline by single crystal X-ray method. The specimen they used was a volcanic nepheline from Monte Somma, Italy. The obtained structure was derived from the tridymite framework in which all silicon atoms in tetrahedra pointing toward one end of the c-axis are replaced by aluminum atoms, and the valence is compensated by the addition of alkali atoms which occupy the voids. They ascertained that the true formula of nephline is not $NaAlSiO_4$ but $KNa_3Al_4Si_4O_{16}$. Subsequently, Harn and Buerger (1955) refined the approximate structure of the volcanic nepheline. Fig. 1-4 shows the crystal structure of nepheline. In the figure, one oxygen atom; $O(1)$, ideally fixed on the three-folded axis, actually occupies statistically three off-axis positions. Among the 16 tetrahedral atoms in the unit cell, silicon and aluminum, only the four special positions; $T(1)$ and $T(2)$ are ordered while the remaining twelve general positions; $T(3)$ and $T(4)$ are disordered.

Smith and Tuttle (1957, 58) determined the variation of the cell dimensions of solid solution between nepheline and kalsilite. In the course of the investigation, they developed an X-ray method for determining the $KAlSiO_4$ content of synthetic nepheline of composition $(Na,K)AlSiO_4$. Smith and Sahama (1954) applied this X-ray method on natural nephelines containing possibly excess silica and certain substituted atoms like Ca and Fe. Through this method they obtained the composition of some natural nephelines. Smith and Tuttle (1957, 58) also studied the phase equilibrium in the system of Ne-Ks series and proved the presence of a miscibility gap. Thus it was verified that $KNa_3Al_4Si_4O_{16}$ was not a single composition but a compound in the solid solution of Ne-Ks series.

Sahama (1962) studied the variation of the optical properties of several nephelines from different geological environments, from room temper-

ature up to 900°C, and distinguished two types of the optical property caused mainly by ordering or disordering. All plutonic nepheline studied by him belongs to the order form whereas volcanic nephelines range from the order form to the disorder form. It was suggested that the degree of ordering in the distribution of the silicon and aluminum cations in the tetrahedra would be variable according to the condition of formation by analogy with that of feldspar.

Dollase (1970) reported the results of least-squares refinement of a plutonic nepheline with composition of $K_{1.4}Na_{5.5}Ca_{0.3}Al_{7.5}Si_{8.5}O_{32}$ from Larvik, Norway. The refinement indicated an intermediate degree of ordering of silicon-aluminum atoms on the four independent tetrahedral sites ($T(1)$, $T(2)$, $T(3)$ and $T(4)$) and confirmed the normal occupancy of $O(1)$ on an off-axis positions. He rationalized the observed positional disorder of $O(1)$, the extent of the common solid solution of silicon replacing aluminum, and the probable location of the excess silica in the structure.

Forman and Peacor (1970) refined the crystal structure of a gneissic nephline with composition of $K_{1.32}Na_{5.64}Ca_{0.36}Al_{7.93}Si_{8.07}O_{32}$, from Bancroft, Ontario, using intensity data measured at temperatures approximately 10°, 200°, 400°, 600° and 900°C, and again at 10°C after heating. They recognized no irreversible changes in the structure of nepheline before and after heating, that is, the presence of the disordered oxygen $O(1)$ at all temperatures and almost complete ordering of silicon-aluminum atoms in all four tetrahedral sites. Thus the structure of a plutonic nepheline and a gneissic nepheline was established in detail, whereas the minute structure of a volcanic nepheline remained to be solved except for the approximate model proposed by Hahn and Buerger (1955).

Simons and Peacor (1972) refined the structure of a nepheline with composion of $K_{1.18}Na_{4.46}Ca_{0.91}$
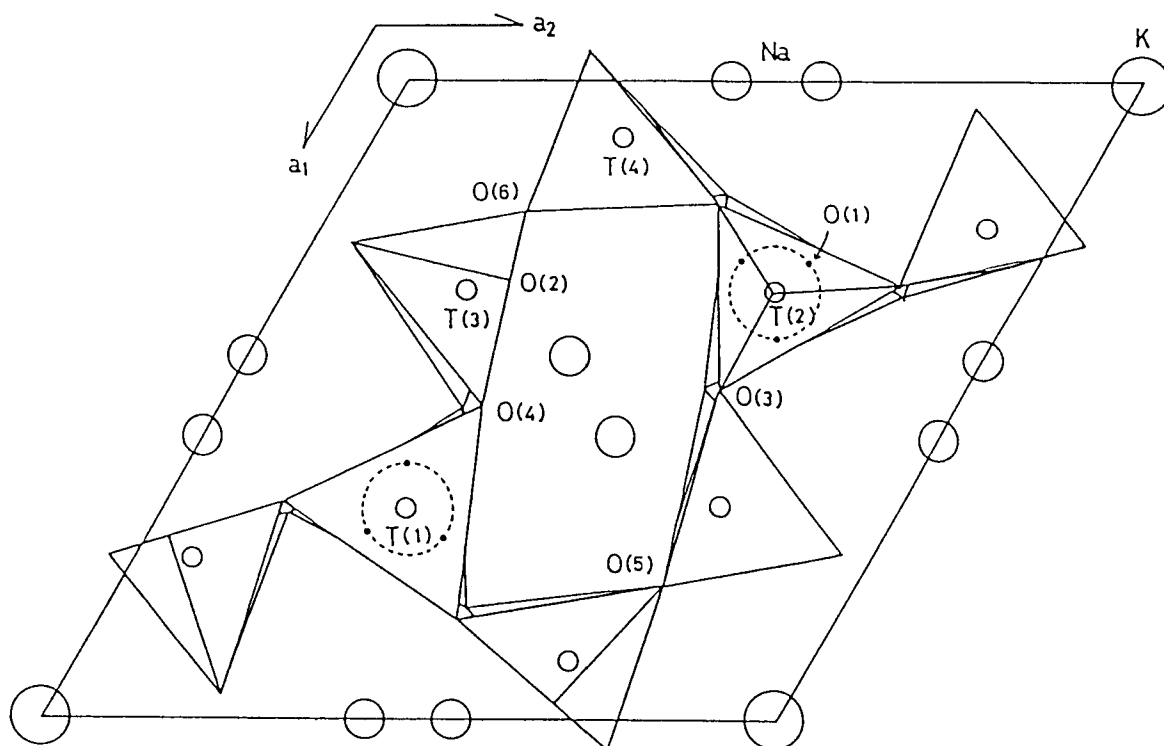
Fig.1–4: (001) projection of the nepheline structure (Harn & Buerger, 1955).

Table 1–1: Natural and synthetic phases of nepheline.

Phase(locality)	Composition	a [Å]	c [Å]	references
Monte Somma (Italy)	$K_{1.28}(Na_{5.36}Ca_{0.28})(Al_{7.92}Si_{8.08}O_{32})$	10.000	8.381	Simons & Peacor (1972)
Larvik (Norway)	$K_{1.4}(Na_{5.5}Ca_{0.3})(Al_{7.5}Si_{8.5}O_{32})$	10.007	8.385	Dollase (1970)
Bancroft (Ontario)	$K_{1.32}(Na_{5.64}Ca_{0.36})(Al_{7.93}Si_{8.07}O_{32})$	9.993	8.374	Foreman & Peacor (1970)
Synthetic	$K_{0.96}Na_{0.96}(Na_{6.00})(Al_{7.92}Si_{8.08}O_{32})$	9.989	8.380	Gregorkiewitz (1980)
Larvik (Na^+ exchanged)	$Na_{1.5}(Na_{5.8}Ca_{0.1})(Al_{7.5}Si_{8.5}O_{32})$	9.968	8.356	Dollase & Thomas (1978)
Synthetic (hydrothermally)	$K_{0.24}(Na_{6.00})(Al_{6.24}Si_{9.75}O_{32})$	9.964	8.360	Dollase & Thomas (1978)

$Al_{7.78}Si_{8.30}O_{32}$ from a volcanic environment (Monte Somma, Italy). The same specimen had been examined by Buerger *et al.* (1954). They proved the existence of an oxygen atom O(1) occupying an off-axis position as indicated by Harn and Buerger (1955). However, Simons and Peacor (1972) showed the considerable disorders of silicon–aluminum on T(1) and T(2) sites (special positions) and the order of silicon–aluminum on T(3) and T(4) sites (general positions), and the results were against to those of Hahn and Buerger (1955).

Dollase and Peacor (1971) examined the degrees of silicon-aluminum ordering existing in some nephelines from different geologic environments and synthetic products. The examined specimens were from Larvik, Norway (plutonic), Bancroft, Ontario (gneissic; before and after heating), Monte Somma, Italy (volcanic), and a Na-exchanged nepheline. They pointed out that the degree of disordering would be increased in the sequence of gneissic–plutonic–volcanic origin, and they confirmed the results by heating experiments. The four independent tetrahedral sites can be divided into two pairs, T(1) & T(2) and T(3) & T(4). The former is always less ordered than the latter. They also pointed out that temperature factors were high for all atoms in nephelines regardless their origin. Simmons and Peacor (1972) explained the fact by the domain structure, which was described in terms of vacancies at the potassium sites and the off-axis displacement of O(1) atoms.

In Table 1 1, chemical composition and lattice parameters of natural and synthetic nephelines reported in the previous literatures are summarized.

Sahama (1958) investigated nephelins from Iivaara, Finland by single crystal X-ray methods and observed weak extra reflections in addition to the strong reflections which corresponds to the ordinary nepheline structure with $a = 10$ and $c =$

8.4 Å. He indicated that the ordinary nepheline cell was a pseudo-cell and the true cell corresponding to these weak extra reflections was considerably larger($a = 17.4$ and $c = 76$ Å) than the ordinary nepheline cell. McConnell (1962), in an electron and X-ray diffraction study of nepheline from a wide range of paragenetic environments, found the presence of additional weak maxima of scattered intensities, which became noticeably diffuse through heat treatment at 200°C, implying a structural transition. In order to explain the weak extra reflections, a domain model has been proposed by Parker (1972), who described that the nepheline structure had a supercell within the domains whose stacking sequence were ABCABC··· or ABACABAC··· along the c-axis. He also suggested that the formation of the supercell and the domains would be caused by the ordering of such atoms as O(1) among three equivalent positions in the average subcell. This domain structure of nepheline might be related to the inversion.

Smith and Tuttle (1957, 1958) described four polymorphs of the compound near $NaAlSiO_4$ composition: high-carnegieite (cubic, stable from the liquidus down to 1,250°C), high-nepheline (orthorhombic, stable between 1,250° and 850°C), low-nepheline (hexagonal, stable between 850°C and the room temperature), and low-carnegieite (low-symmetry, obtained at 690°C by quenching). Later, Cohen and Klement (1976) studied the effect of pressure on reversible transitions in nepheline and carnegieite. They found that the inversion temperature of high–low carnegieite increased from about 707°C at 1 bar with inceasing pressure and that of high–low nepheline increased from about 872°C at 1bar with inceasing pressure. They also found rapidly reversible transition in nepheline near 185°C at 1bar.

Henderson and Roux (1977) studied subpotassic nephelines with less than 2.5 mol percent Ks using an X-ray powder diffractometer

and they found that sub-potassic nephelines had different structures depending on their composition and temperature. Henderson and Thompson (1980) performed further investigation about sub-potassic nephelines by means of differential scanning calorimetric and high temperature X-ray diffraction methods. They classified nephelines into four types according to their composition and found the existence of displacive inversion points. Type-H nephelines (> 2.5 % Ks) show no inversion and are hexagonal at room temperature. On the other hand, sub-potassic nephelines have an orthorhombic superstructure and some of them invert to the hexagonal structure determined by Hahn and Buerger (1955). Sub-potassic nephelines are devided to type-A, B and C. Type-C nephelines (0.7 to 2.5 % Ks) have a single inversion point which corresponds to the orthorhombic-hexagonal inversion, $e.g.$, nepheline containing 1.6 % Ks, with $a = 10.000$, $b = 17.254$, $c = 24.988$ Å, inverts to the hexagonal structure near 92°C. The temperature of the inversion is raised with decreasing Ks content. Type-B nephelines (< 0.7 % Ks) have two inversion points, of which the lower temperature corresponds to the orthorhombic-hexagonal inversion found in type-C and the upper to the low symmetry(second phase) hexagonal inversion. The details of this second phase are unknown. Type-A nephelines (pure-Ne) have no displacive inversion. Henderson and Thompson (1980) proposed that the orthorhombic superstructure in sub-potassic nephelines ascribed to the reversible collapse of the framework around the large cavities which were occupied by smaller sodium atoms instead of larger potassium atoms. Further, McConnell (1981) concluded that the intensities of the extra reflections of sub-potassic nephelines changed on heating, and suggested that reversible transitions would be attributed to the process of disordering of potassium atoms and vacancies in the large cavities of the framework.

The site preference of the alkali positions in the nepheline structure has been reported by Dollase and Thomas (1978). According to them, the order of the site preference in the large cavities (normally occupied by potassium atoms) is K > □(vacancy) ≫ Na, and that in the small cavities(normally occupied by sodium atoms) is Na > (Ca) ≫ K > □.

As mentioned above, the precise structure of nephelines has been investigated in detail by many investigators, and it has been clarified that the ordering of silicon–aluminum atoms on the four tetrahedral sites varies with the formation conditions of nephelines, and that the composition of nephelines plays an important role on the site occupancy or the site preference. However, the cause of the occupation of O(1) atoms on the off-axis positions is still unknown, and it is not clear how the superstructure or the domain structure related to the extra reflections are controlled. Even so, the reported structural properties of nephelines is effective on the consideration of KAlSiO₄ minerals (kalsilite, kaliophilite, and orthorhombic KAlSiO₄) which are the members of nepheline–kalslite group.

2 Kalsilite

2.1 Research history

In the course of the investigation of a series of volcanic rocks from the southwest Uganda, Holmes (1942) found a new mineral whose optical properties were similar to those of nepheline. At first this mineral was considered to be kaliophilite based on the chemical analysis. However, the result of X-ray analysis indicated that the mineral is not kaliophilite but a new polymorph of KAlSiO₄.

Bannister and Hey (1942) examined thoroughly this new mineral by microscopic and X-ray methods. The single crystal X-ray photographs re-

vealed that the mineral was hexagonal and possessed cell dimensions, $a = 5.17$, $c = 8.67$ Å, and that the space group was obviously $P6_322$ because of the missing of $00l$, l-odd reflections. They proposed the name 'kalsilite' to this new mineral after its chemical composition including K, Al, and Si. Later, Jay and Andrew (1947) found kalsilite in a blast-furnace linings and reported the chemical compositions and X-ray powder data($a = 5.160$, $c = 8.702$ Å). Rigby and Richardson (1947) also described this new mineral from the same origin.

Bannister, Sahama and Wiik (1952) examined a nepheline-like mineral occurring in a high potash-rich lava at San Venanzo, Umbrica, Italy, and concluded that the mineral was kalsilite on the basis of the chemical analysis together with the optical properties. Cell dimensions($a = 5.13$, $c = 8.657$ Å) of the phase were also measured by these authors.

Smith and Tuttle (1957) synthesized kalsilite by hydrothermal method from mixtures of composition Ne0 (100 % Ks) and Ne10 (10 % Ne 90 % Ks). The measured cell dimensions ($a = 5.159$, $c = 8.703$ Å) for this synthetic kalsilite crystallized from Ne0 agreed well with the values obtained by Jay and Andrew (1947). The cell dimensions of the synthetic kalsilite are slightly larger than those of the natural kalsilite(Bannister et $al.$, 1952). This discrepancy may be ascribed to the slight variation of the composition in the natural kalsilite including substituted atoms (sodium or calcium at the site of potassium, iron at the site of aluminum).

The crystal structure of kalsilite was considered to be related with those of $BaAl_2O_4$ ($a = 5.21$, $c = 8.67$ Å) and $KLiSO_4$ ($a = 5.13$, $c = 8.60$ Å; Bradley, 1925) by Claringbull and Bannister (1948). They presumed that the structure was derived from hexagonal tridymite, the constituent tetrahedral atoms were disordered because of the space group $P6_322$, and the oxygen atoms connecting tetrahedral atoms showed a straight linkage.

Smith and Sahama (1957) carefully studied a kalsilite from Nyiragongo, Congo, by means of single crystal X-ray method. The kalsilite has weak and diffuse reflections in addition to strong and sharp ones. They showed that a new unit cell took a position rotated at 30° from the original cell around the c-axis, resulting expanse of the a-axis by $\sqrt{3}$. It should be noted that the superstructure could be present similarly to the nepheline structure (Sahama, 1958). The intensity of the diffuse reflections, however, varied from a crystal to another, and these reflections disappeared by heat treatment up to 600°C. They concluded that the diffuse reflections were caused by the ordering of tetrahedral atoms and suggested possibility of the two types of kalsilite, $i.e.$, o-kasilite (ordered form, $a = 8.9$ Å) and d-kalsilite(disordered form, $a = 5.15$ Å). The o-kalsilite has a supercell taking a position rotated at 30° in relation to the d-kalsilite cell.

Further, Sahama (1960) examined petrologically kalsilite-bearing rocks from the same locality studied by Smith and Sahama (1957). He found kalsilites in the rock both as complex nepheline-kalsilite phenocrysts and as grains in the fine-grained groundmass. The complex phenocrysts indicated a continuous series of progressing exsolution.

A three dimensional refinement of kalsilite was performed by Perrota and Smith (1965). They proved that the structure of kalsilite ($a = 5.161 \pm 0.004$, $c = 8.693 \pm 0.005$ Å) can be explained as that of tridymite by rotating the tetrahedra in the (001) plane. Kalsilite, $K_{1.91}Na_{0.03}(H_2O)_{0.11}Al_{1.93}Si_{2.03}Fe_{0.05}O_8$, was described from the same locality by Smith and Sahama (1957). However, Perrota and Smith could not observed diffuse reflections. Through this refinement they confirmed that the silicon and alu-

minum atoms could be ordered because the tetrahedral distances (T–O) are 1.61 and 1.74 Å, respectively, and concluded that the space group of kalsilite is not $P6_322$ but $P6_3$. They also confirmed that an oxygen atoms connecting the silicon and aluminum atoms statistically occupied three fold degenerate positions displaced by 0.25 Å from the ideal positions on triad axes, and the bond angles were less than 180° and decreased to 163°. The same structure is also observed in nepheline. They suggested the following three possibilities, in order to explain the existence of the diffuse reflections observed by Smith and Sahama (1957).

1. Ordering of the displacements of the oxygen atoms from the triad axis.

2. Ordering of substitutions such as Na or H_2O in the alkali site formerly occupied by K.

3. Presence of alteration product.

They concluded that the existence of the diffuse reflections could not be considered in respect of the ordering of tetrahedral atoms but might be explained by the displacements of the oxygen atoms.

Tables 2–1 and 2–2 give the atomic parameters and interatomic distances of natural kalsilite reported by Perrota and Smith (1965), and Fig. 2–1 shows the scheme of the crystal structure of kalsilite elucidated by them.

Later, Dollase and Freeborn (1977) were successful to obtain kalsilite by alkali exchange of nepheline in molten KCl. They carefully measured intensities of reflections of the type hhl, l-odd for various single crystals. The intensities were different from a crystal to another. The measured cell dimensions($a = 5.153\pm0.005$, $c = 8.682\pm0.009$ Å) were close to those of natural kalsilite (Perrota and Smith, 1965), and the refined crystal structure, given in Table 2–3, revealed the same structure as that of natural kalsilite including ordered tetrahedral atoms and a disordered oxygen atoms

which link tetrahedral atoms in the (00l) plane. However, the crystal used for the structure analysis exhibited no observable hhl, l-odd reflections. The fact was attributed to domain structure.

In order to clarify the kalsilite structure, formation mechanism of the domain structure is significant. In this paper, experiments to synthesize kalsilite crystals were carefully carried out under the hydrothermal condition. Obtained single crystals were used for X-ray intensity measurements, and the crystal structure of kalsilite was refined by three dimensional counter-measured intensity data. Throughout the investigation, the calculations were carried out at the Computer Center of Okayama University, using the modified programs of UNICS (Sakurai, 1971).

2.2 Synthesis of kalsilite

Synthesis of kalsilite was carried out by hydrothermal method. Starting materials were special grade reagents of activated alumina (Al_2O_3), silica gels (SiO_2), and potassium carbonate (K_2CO_3). K_2CO_3 was added more excessively than the content of the stoichiometric KAlSiO₄. In addition, the synthesis was carried out also from the starting materials which contained Na_2CO_3 taking place of K_2CO_3, where the content of K_2CO_3 was still excess enough to produce KAlSiO₄. Hydrothermal syntheses were performed using the test-tube type equipment (modified from Luth and Tuttle, 1963) under the condition of 600°C, 1,000 kg/cm² within the duration of 14 days. Obtained crystals were colourless with euhedral forms. The crystal habits were varied with the degree of excess K_2CO_3 in the starting materials and showed platy, glanular, and needle-like forms. The condition and the result of the hydrothermal syntheses are shown in Table 2–4.

Table 2-1: Atomic parameters and anisotropic temperature factors
of natural kalsilite (Perrota & Smith, 1965).

Atom	x	y	z	$B_{eq.}$	B_{11}	B_{22}	B_{33}	B_{12}	B_{23}	B_{13}
K	0	0	0.25	1.18(3)	0.0148	0.0148	0.0034	0.0074	0	0
Al	1/3	2/3	0.055(1)	0.52(7)	0.0063	0.0063	-0.0005	0.0032	0	0
Si	1/3	2/3	0.437(1)	0.37(4)	0.0044	0.0044	0.0018	0.0022	0	0
O(1)	0.617(1)	0.013(1)	0.995(2)	1.01(5)	0.0074	0.0084	0.0095	0.0039	-0.0020	-0.0016
O(2)	0.334(3)	0.716(3)	0.259(4)	0.94(25)	0.0572	0.0572	-0.0005	0.0286	0	0

Table 2-2: Interatomic distances of natural kalsilite
(Perrota & Smith, 1965).

Atom	distances [Å]
K-O(1)	2.992
K-O(1)'	2.929
K-O(2)	2.767
mean K-O	2.896
Al-O(1)	1.729
Al-O(2)	1.787
mean Al-O	1.744
Si-O(1)	1.624
Si-O(2)	1.570
mean Si-O	1.611

Table 2-3: Atomic parameters and anisotropic temperature factors
of alkali exchanged kalsilite (Dollase & Freeborn, 1977).

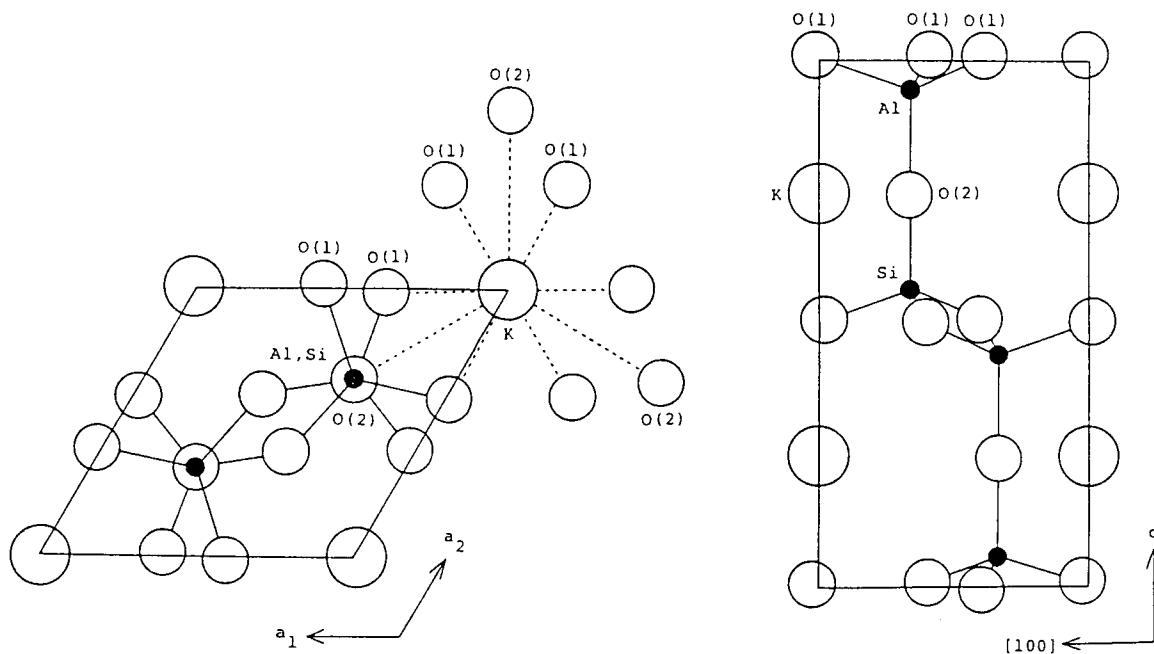| Atom	x	y	z	$B_{eq.}$	B_{11}	B_{22}	B_{33}	B_{12}	B_{23}	B_{13}
K	0	0	0.25	1.67	0.0193	0.0193	0.0045	0.0193	0	0
Al	1/3	2/3	0.056(1)	0.83	0.0110	0.0110	0.0031	0.0110	0	0
Si	1/3	2/3	0.437(1)	0.64	0.0063	0.0063	0.0035	0.0063	0	0
O(1)	0.614(2)	0.019(3)	0.993(3)	–	0.0123	0.0012	0.0117	0.0002	0.0132	0.0109
O(2)	1/3	0.720(3)	0.258(4)	0.9(4)	–	–	–	–	–	–

Fig.2-1: (001) and (100) projections of kalsilite structure
(Perrota & Smith, 1965 ; partly modified by the present author).

Table 2–4: Hydrothermal synthesis of kalsilite.
(Temperature : 600°C , Pressure : 1,000kg/cm^2)

Starting materials Al$_2$O$_3$: SiO$_2$: K$_2$CO$_3$	Rate of cooling [°C/day]	Run time [hour]	Cooling time [hour]	Product(single crystal) volume,form	Sample No.
1 : 2 : 1.00	–	48	–	n , –	2–1
	12	406	406	m , P	2–3
	5	336	240	m , H + P	2–4
1 : 2 : 1.50	20	480	240	m , G	6–1
	70	335	71	m , G + H	6–3
	5	336	240	m , G + H	6–4
1 : 2 : 2.00	–	48	–	f , N	3–1
	50	104	95	s , G + N	3–2
	5	336	240	m , H	3–6
1 : 2 : 3.00	–	48	–	n , –	4–1
	50	290	246	s , G	4–2
1 : 2 : 1.75	70	335	71	f , G + H	7–1
	5 (600–550°C)	306	306	m , H + G	7–2
	5 (550–500°C)	312	312	m , H + G	7–3
	5 (500–450°C)	312	312	m , H + G	7–4
1 : 2 : 1.25 + Na$_2$CO$_3$ 0.50	70	335	71	m , G	8–1

volume : n (no) , f (few) , s (several) , m (many)

form : N (needle) , P (platy) , G (granular) , H (hexagonal pillar)

Table 2–5: The X–ray powder data of synthetic kalsilite.

d(obs.) [Å]	I(obs.)	h k l	d(calc.) [Å]
4.363	23	0 0 2	4.345
3.985	54	1 0 1	3.969
3.116	100	1 0 2	3.113
2.584	50	1 1 0	2.576
2.477	12	1 1 1	2.469
2.437	10	1 0 3	2.429
2.236	4	2 0 0	2.231
2.223	10	1 1 2	2.216
2.177	20	0 0 4	2.172
2.166	6	2 0 1	2.161
1.990	5	2 0 2	1.984
1.958	3	1 0 4	1.953
1.929	4	1 1 3	1.925
1.771	3	2 0 3	1.767
1.665	4	1 1 4	1.661
1.660	5	2 1 1	1.655
1.623	7	1 0 5	1.619
1.575	7	2 1 2	1.572
1.551	2	2 0 4	1.556
1.490	8	3 0 0	1.487
1.461	3	2 1 3	1.457
1.374	3	2 0 5	1.371

2.3 Measurements of cell dimensions and intensities

The powder diffraction data of synthetic kalsilites shown in Table 2–5 were collected on a Rigaku powder diffractometer using $CuK\alpha$ radiation ($\lambda = 1.5418$ Å). The specimen was mixed with a small amount of silicon powder as an internal standard. The powder diffraction data of these synthetic kalsilites exhibit almost the same values with each other ($a \approx 5.16$, $c \approx 8.71$ Å). Kalsilites having the same parameters were also synthesized from starting materials containing both K_2CO_3 and Na_2CO_3, as shown at Sample No.8–1 in Table 2–4. This compound contains potassium alone as alkali atoms, and the fact suggests that potassium atoms occupy the alkali sites more easily than sodium atoms. The fact also supports the site preference proposed by Dollase and Thomas (1978).

Crystals (Sample No.7–4 in Table 2–4) were selected for X-ray intensity measurements. Morphology of the crystals are hexagonal prism elongated along the c-axis and had approximate dimensions $0.2 \times 0.2 \times 0.5$ mm. The diffraction symmetry were examined based on Weissenberg photographs taken by $CuK\alpha$ radiation. The space group was confirmed to be $P6_3$ or $P6_322$. Three-dimensional intensities were collected on an automated four-circle diffractometer using the $2\theta - \omega$ scan technique and $MoK\alpha$ radiation ($\lambda = 0.70926$ Å) with graphite monochromator. 373 reflections with intensity of $I>3\sigma$ above background were classified as observed. Intensities were converted to the structure factors by applying the Lorentz–polarization correction. The absorption corrections were not used because the dimensions of crystals were much smaller than $1/\mu$ (μ : absorption coefficient $= 1.705$ mm^{-1}). The crystal data, such as cell dimensions and their standard deviations measured by the same diffractometer, are listed in Table 2–6. The values of cell dimensions($a = 5.151 \pm 0.005$, $c = 8.690 \pm 0.008$ Å)

are close to those reported by previous investigators (Perrota and Simth, 1965 / Dollase and Freeborn, 1977).

2.4 Structure refinement

Five cycles of full-matrix least-squares calculation were carried out with the space group $P6_3$, using the positional parameters of the natural kalsilite (Table 2–1) obtained by Perrota and Smith (1965). Atomic parameters and isotropic temperature factors were approximately converged to the same values with those of the natural kalsilite or those of the alkali-exchanged kalsilite (Table 2–3) given by Dollase and Freeborn (1977). 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. Therefore, the multiplicities between the O(1) atoms and its mirror equivalent oxygen atoms were refined together with other parameters, and the structure was converged to the final R-value of 0.084 for anisotropic temperature factors, giving equal weights to all reflections. The rather high R-value is probably due to the extensive disorder of the O(1) atoms (Andou and Kawahara, 1984).

The obtained final positional parameters and temperature factors of synthetic kalsilite are shown in Table 2–7 and interatomic distances are listed in Table 2–8. Scattering factors corresponding to neutral atoms were used throughout the calculations (International Tables for X-ray Crystallography, 1974).

2.5 Description of the structure and discussion

Fig. 2–2 shows the (001) projections of the structure of the 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

Table 2-6: 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	$d_{calc.}$=2.64 g/cm³

Table 2-8 Interatomic distances of synthetic kalsilite.

Atom	distances [Å]
K–O(1)	2.92(2)
K–O(1)'	3.00(2)
K–O(2)	2.84(4)
mean K–O	2.92
Al–O(1)	1.69(1)
Al–O(2)	1.73(5)
mean Al–O	1.70
Si–O(1)	1.65(1)
Si–O(2)	1.60(5)
mean Si–O	1.64

Table 2-7: Atomic parameters and anisotropic temperature factors of synthetic kalsilite.

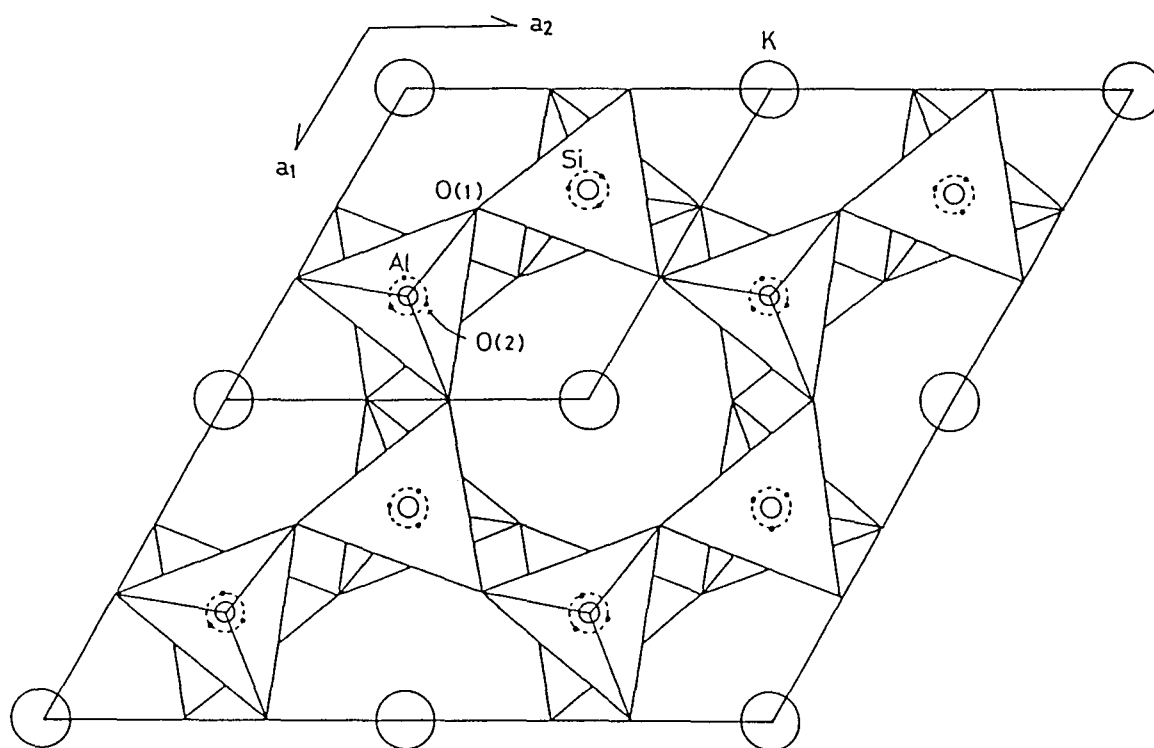| Atom	x	y	z	$B_{eq.}$	B_{11}	B_{22}	B_{33}	B_{12}	B_{23}	B_{13}
K	0	0	0.25	1.25(5)	0.0164	0.0164	0.0039	0.0082	0	0
Al	1/3	2/3	0.054(2)	0.74(12)	0.0111	0.0111	0.0015	0.0056	0	0
Si	1/3	2/3	0.436(1)	0.45(9)	0.0028	0.0028	0.0030	0.0014	0	0
O(1)	0.610(2)	0.005(2)	0.993(2)	1.4(2)	0.0127	0.0088	0.0086	0.0062	-0.0033	-0.0039
O(2)	0.350(8)	0.713(4)	0.252(6)	1.0(3)	–	–	–	–	–	–

Fig.2-2: (001) projection of the synthetic kalsilite structure (four unit cells).

to the c-axis and by one O(2) atom in the direction along the c-axis, constructing tridymite-like frameworks. O(2) atoms are statistically distributed over three sites displacing slightly from the ideal positions. This structure is almost the same to that of the natural kalsilite. O(1) atoms, however, are disordered partly between two sites, which are related by a mirror plane perpendicular to the a-axis. This signifies the domain structure of the synthetic kalsilite, as already revealed in the alkali-exchanged kalsilite by Dollase and Freeborn (1977).

Fig. 2-3 shows the framework structure of silicon–aluminum tetrahedra of kalsilite. The structure has two types, **(a)** and **(b)**. The two are related with each other by mirror planes through longer diagonals of the unit cell, or normal to the a-axis. The domain structure of kalsilite is constructed of these two types of the structures. The structural relation between **(a)** and **(b)** types is the same as in the case of twinning, in which the twin lattice coincides with the original lattice. This twinning relation corresponds with merohedry in the classification of twins proposed by Friedel (1926).

Fig. 2-4 shows the variation of the calculated structure factors of the type hhl, l-odd against the continuous change of the ratio of the domain volume ((**a**) type : (**b**) type). Volumes are normalized to the same scale so that the sum of the type hhl, l-even becomes constant for the change of the domain ratio. As is evident in the figure, arrangement of these lines is symmetrical at the center. Therefore it is impossible to distinguish two domain ratios ($e.g.$, 1 : 2 and 2 : 1) even with the aid of the structure factors of the type hhl. However, the structure factors of the type hkl and khl are different with each other, so with the aid of them it is possible to distinguish these domain ratios. Actual values measured for three different crystals are plotted in Fig. 2-4. It is noted that

different crystal have different domain ratios.

Dollase and Freeborn (1977) interpreted that the domain structure could be formed through the transformation from nepheline to kalsilite by tetrahedral rotation and by this rotation successive (001) layers underwent opposite-sense rotation. However, this interpretation can not be applied to the present kalsilite synthesized hydrothermally. The present synthetic kalsilite does not have any diffuse streaks parallel to c^*, while the alkali-exchanged kalsilite has them. This can be interpreted as follows. Because the alkali-exchanged kalsilite (Dollase and Freeborn, 1977) is produced from nepheline without breaking the tridymite-like framework, the domain boundaries occur more easily at the plane normal to the c-axis than at the plane parallel to the c-axis. Therefore it is possible that the domain thickness along the c-axis is to be $nc/2$ (n=integers) yielding the diffuse streaking. On the other hand, present synthetic kalsilite is produced from non-crystalline materials. The domain boundaries could occur at the plane normal to the c-axis as much as at the plane parallel to the c-axis and probably the latter would be more frequent.

In this way the synthetic and alkali-exchanged kalsilite exhibit very similar structural characteristics but the origin of the domain structure might be quite different with each other. It is likely that kalsilite has the inversion point at the temperature at which the domain structure is constructed. In conclusion, the domain structure of kalsilite is ascribed to the displacive high–low inversion of the structure (Andou and Kawahara, 1982). Such type of inversion is often found in quartz, tridymite, leucite and others ($e.g.$, Nukui and Nakazawa, 1980).

2.6   Inversion of kalsilite structure

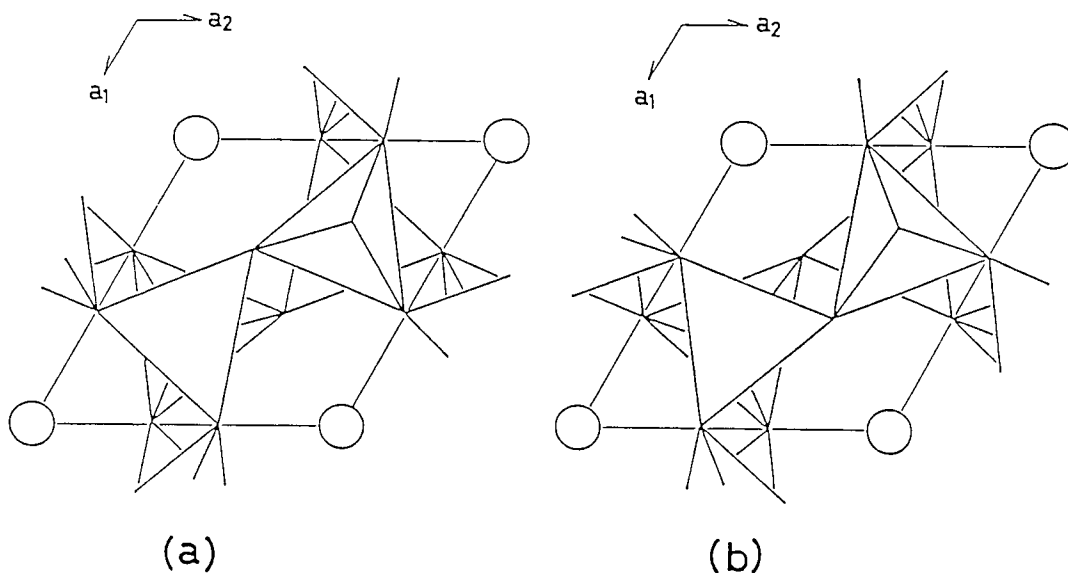The high temperature X-ray powder photographs were taken with a Weissenberg camera in which

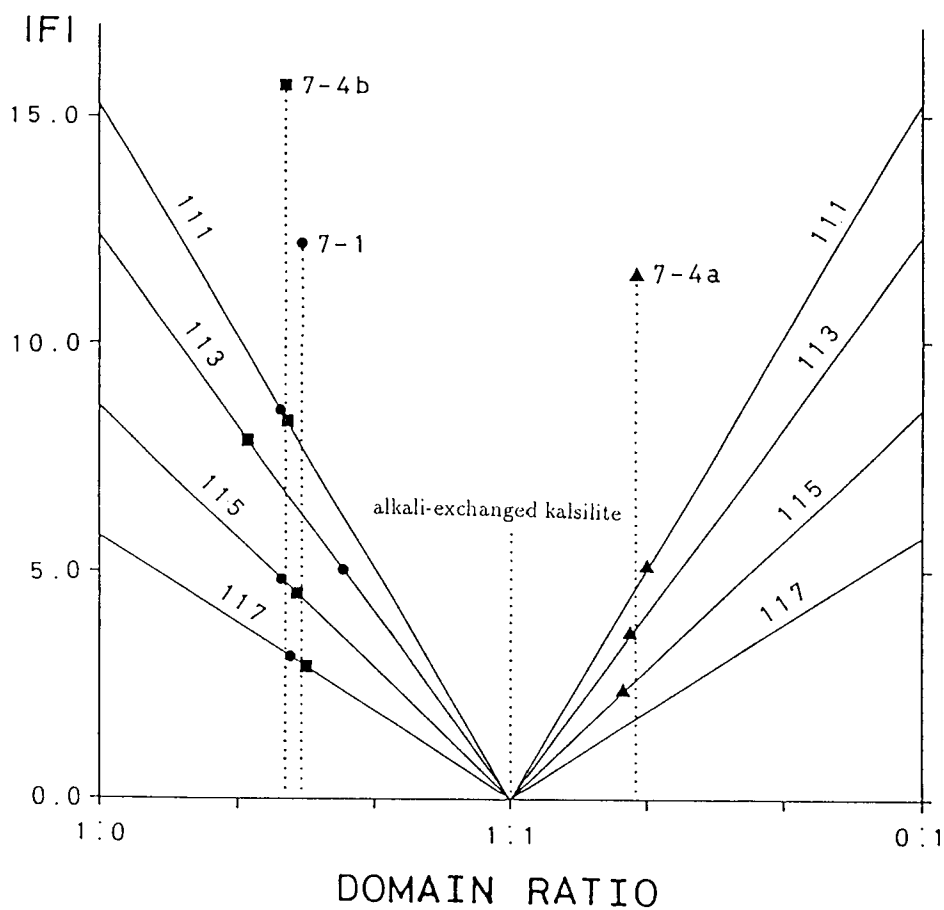Fig.2-3: Two types of the kalsilite structure.

Fig.2-4: Structure factors of reflections of the type hhl, l-odd for four kinds of kalsilite crystal. Each line of structure factors is varied as a function of domain ratio.

a small electric furnace was set up, using CuKα radiation. The powder specimen of kalsilite synthesized hydrothermally (600°C, 1,000 kg/cm^2, 7 days) was sealed in a thin quartz glass capillary (ϕ = 0.5 mm) together with a small amount of silicon powder and fixed on a goniometer head. The temperature was measured by chromel–alumel thermocouples, whose scales of the millivoltmeter were calibrated by the melting point of Zn (419°C) and Ag (961°C) metals.

The measurement was carried out from room temperature up to 1,000°C. The heating and cooling experiments were repeated on the same powder specimen in this temperature range. Below 865°C, no clear change of the observed powder pattern was recognized but slight shift of the pattern was recognizable due to thermal expansion. Above 865°C, the pattern revealed clear difference. The change of the pattern at 865°C was characteristically reversible, indicating certain inversion. Fig. 2–5 is the X-ray powder photographs and shows the noticeable change of 111 reflection at 860°C and 870°C. The structure found in the X-ray powder pattern above 865°C was refered to 'high-kalsilite'.

The cell dimensions (870°C) were refined by the program RSLC3 of UNICS (Sakurai, 1971) using 13 reflections obtained by high temperature X-ray powder photographs. The instrumental errors of the diffractometer were corrected by using silicon powder contained as an internal standard. The values of a = 5.30(1) and c = 9.65(1) Å were obtained.

2.7   Confirmation of high-kalsilite

The structure of high-kalsilite was assumed first from that of the low-form by rotating the tetrahedra in (001) layers from ditrigonal ring configurations to the hexagonal ones. This configuration yields change of space group from $P6_3$ to $P6_3mc$. The space group will further change to $P6_3/mmc$

if the random distribution of silicon and aluminum atoms are considered. The atomic parameters of the structure were determined geometrically based on the symmetry of the space group of $P6_3mc$ or $P6_3/mmc$. Here, for convenience, the random distribution of silicon and aluminum atoms was assumed. The obtained results are listed in Table 2–9. The values of isotropic temperature factors of these atoms were assumed by making reference to those of nepheline (908°C) investigated by Foreman and Peacor (1970).

In order to confirm the structure of the high-kalsilite determined above, X-ray powder diffraction patterns were measured at temperatures 20°, 600°, 800° and 1,000°C and the results were compared with each other. Fig. 2–6 shows the observed powder patterns at those temperatures. Since the space group changed from $P6_3$ to $P6_3mc$ or $P6_3/mmc$, the pattern observed at 1,000°C lacks hhl, l–odd reflections. In fact, the peak of 111 is moderate strong at temperature lower than 865°C but it is completely absent in the pattern observed above this temperature (see, Fig. 2–6). This powder patterns were simulated also by the computer using the atomic parameters of the high-kalsilite (Table 2–9). The results are shown in Fig. 2–7 together with that of low-form structures. The program (PPDP) used for the calculation was newly written by the present author.

The scheme of the structure of high-kalsilite is shown in Fig. 2–8 together with that of low-form structures. As seen in the figure and, the positions of O(1) atoms in the low-form occupy two general positions and O(1) atoms in the high-form occupy one special position on mirror planes parallel to the c-axis. The two kinds of Si–O and Al–O tetrahedra have been already proved to be arranged orderly in the low-form. If the transition from low- to high-form causes only the slight rotation of Si(Al)–O tetrahedra and the displacement of O(1) atoms, the distribution of Si–O and Al–O
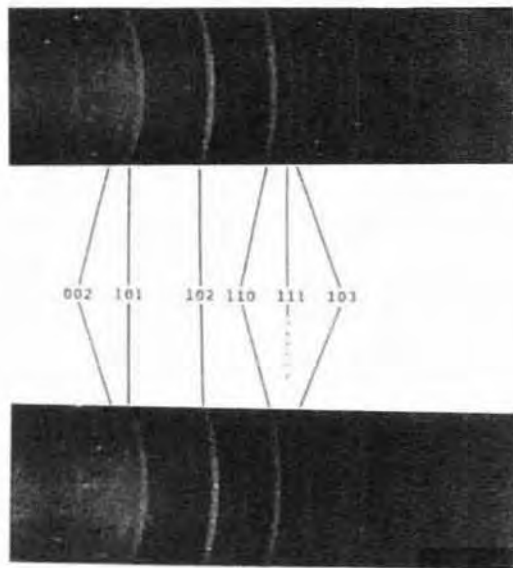
Fig.2-5: The comparison of the observed
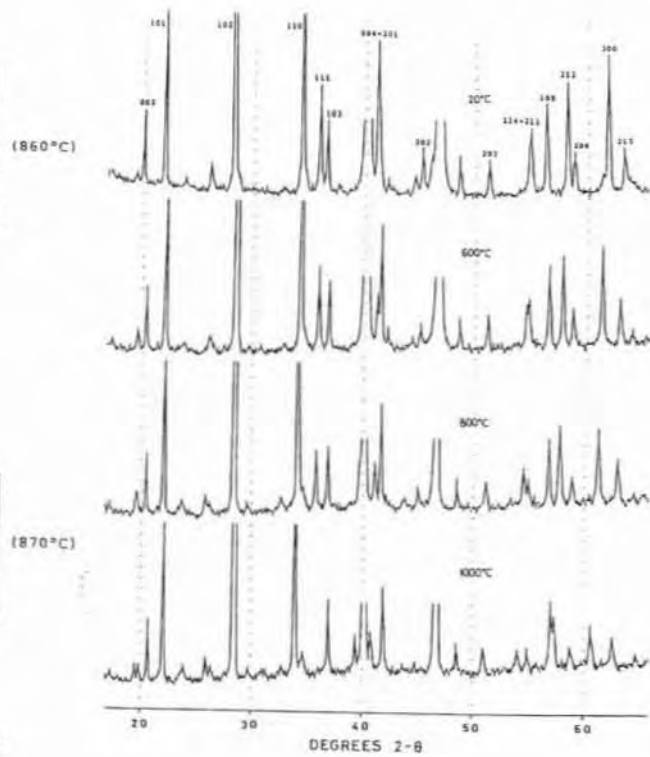powder pattern at 860°C(upper)
and 870°C(lower).

Fig.2-6: The powder patterns measured at 20°,
600°, 800°, and 1,000°C.
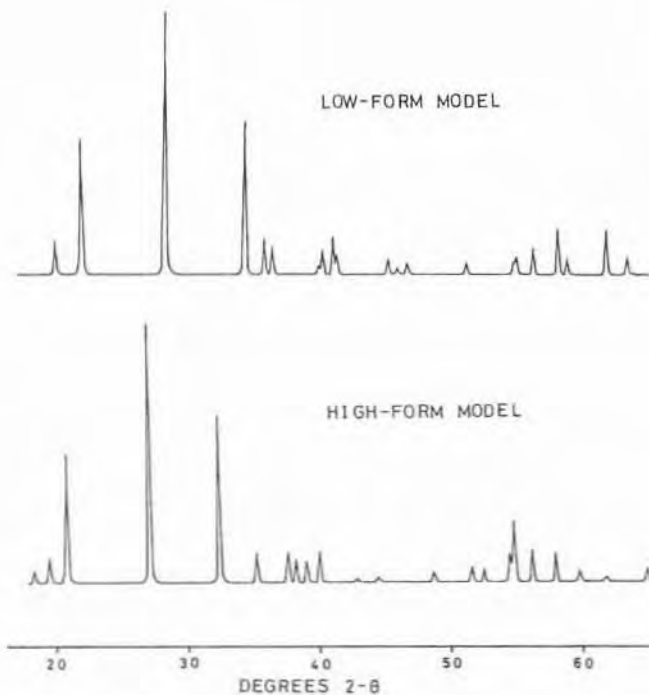Some unindexed peaks belong to that
of Pt.

Fig.2-7: Simulated powder pattern of low-
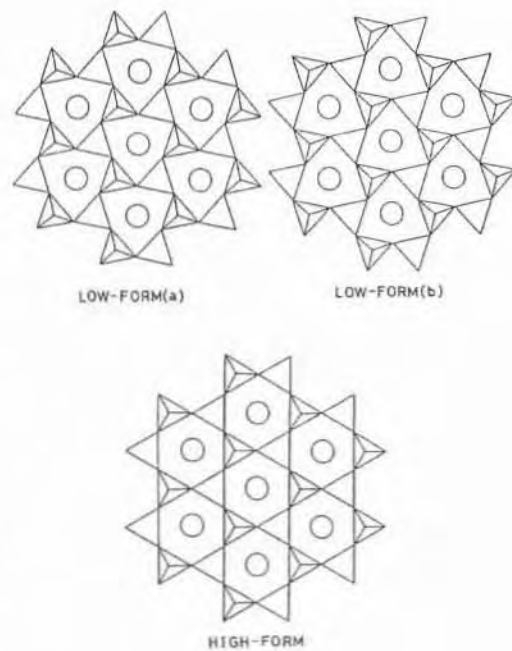and high-form model.

Fig.2-8: The schema of low-form and
high-form structures.

Table 2 9: Cell dimensions and atomic parameters
of high-kalsilite calculated assuming the
symmetry of the space group $P6_3/mmc$.

Atom	x	y	z	$B_{eq.}$
K	0	0	1/4	17.0
Al	1/3	2/3	1/16	3.0
Si	1/3	2/3	7/16	3.0
O(1)	1/2	0	0	5.0
O(2)	1/3	2/3	1/4	5.0

Table 2 10: Interatomic distances(870°C)
of assumed high-kalsilite model.

Atom	distances [Å]
K-O(1)	3.42(×12)
K-O(2)	3.06(×3)
mean K-O	3.35
Si(Al)-O(1)	1.62(×3)
Si(Al)-O(2)	1.62(×1)
mean Si(Al)-O	1.62

Number in parentheses indicate multiplicity.

Fig.2-9: The setting of the kalsilite crystal
for the high-temperature experiment.

Table 2-11: Cell dimensions of kalsilite measured at various temperatures.

Temperature [°C]	Time [hour]	a [Å]	c [Å]	V [Å^3]
20	–	5.1521(4)	8.649(4)	198.8(1)
210	20	5.1682(5)	8.662(4)	200.4(1)
400	20	5.1896(3)	8.663(2)	202.1(1)
600	48	5.2148(6)	8.674(6)	204.3(1)
700	4	5.2306(4)	8.655(3)	205.1(1)
800	4	5.2569(7)	8.655(5)	207.1(1)
850	10	5.2673(6)	8.655(5)	208.0(1)
900	3	5.2807(7)	8.629(5)	208.4(1)
950	6	5.2879(5)	8.628(5)	208.9(1)

Table 2-12: Atomic parameters and anisotropic temperature factors of high-kalsilite(950°C).

Atom	x	y	z	$B_{eq.}$	B_{11}	B_{22}	B_{33}	B_{12}	B_{23}	B_{13}
K	0	0	0.25	9.3(4)	0.1004	0.1004	0.0371	0.0502	0	0
Al	1/3	2/3	0.058(4)	2.6(3)	0.0348	0.0348	0.0070	0.0174	0	0
Si	1/3	2/3	0.439(3)	5.7(5)	0.0654	0.0654	0.0205	0.0327	0	0
O(1)	0.506(6)	0.012	0.984(4)	15.1(1.2)	0.2130	0.2130	003185	0.1915	-0.0373	-0.0373
O(2)	0.407(7)	0.741(12)	0.250(6)	3.2(6)	–	–	–	–	–	–

Table 2-13: Interatomic distances of high-kalsilite(950°C).

Atom	distances [Å]
K-O(1)	3.50(3)
K-O(1)'	3.33(4)
K-O(2)	2.72(6)
mean K-O	3.12
Al-O(1)	1.70(4)
Al-O(2)	1.70(6)
mean Al-O	1.70

Atom	distances [Å]
Si-O(1)	1.53(4)
Si-O(2)	1.68(6)
mean Si-O	1.57

tetrahedra in the high-form would be still ordered and the space group of high-form would be $P6_3mc$. On the other hand, if many structural misfits are present in the plane parallel to (001) in the low-form and the considerable amount of domain parts suffer the rotation of 60° about three-fold axis at the time of inversion, the space group of high-form would be $P6_3/mmc$ which corresponds to the symmetry of disordered high-kalsilite.

The values of interatomic distances (at 870°C) of the assumed high-kalsilite is shown in Table 2-10. Because the random distribution of silicon and aluminum atoms is assumed in this model, the values of interatomic distances of Si–O and Al–O tetrahedra are the same. The potassium atoms are surrounded by three O(2)=3.1 Å and twelve O(1)=3.4 Å, and the coordination number becomes fifteen.

2.8 Single crystal analysis

A kalsilite crystal used for the structure refinement of the high-form was also a material synthesized by hydrothermal method (Kawahara, Andou, Okuno and Marumo, 1987). The crystal used for X-ray intensity measurements was the hexagonal prism in shape with approximate dimensions of 0.2 × 0.3 × 0.1 mm, mounted on a silica capillary as illustrated in Fig. 2-9.

Three dimensional intensities were collected on an automated four-circle diffractometer using the $2\theta - \omega$ scan technique and by MoKα radiation with graphite monochrometor. Intensities were collected up to $2\theta=80°$. The temperature was determined by means of chromel–alumel thermocouple placed close to the crystal, and the accuracy is ±10°C. Finally, 115 reflections with intensity of I>3σ above background were observed. They were converted to the structure factors by applying Lorentz–polarization correction. Reflections of 00l, l–odd and hhl, l–odd were extinct statistically. Therefore the space group was confirmed

to be $P6_3mc$ or $P6_3/mmc$ as was assumed previously by the geometrical relationship between the real low-kalsilite and the simulated high-kalsilite.

The cell dimensions were also measured using the same diffractometer. The measurements were carried out at temperatures 20°, 210°, 400°, 600°, 700°, 800°, 850°, 900°, 950°C with an accuracy of ±10°C. Reflections used for the calculation were 002, 00$\bar{2}$, 101, $\bar{1}$11, 102, $\bar{1}$02, $\bar{1}$12, 1$\bar{1}$2, 212, 1$\bar{3}$2, $\bar{3}$22, 21$\bar{2}$, 13$\bar{2}$, $\bar{3}$2$\bar{2}$, 300 and 3$\bar{3}$0. The values for the reflection angles were measured on both sides of 2θ and they were averaged. Table 2–11 lists the cell dimensions at various temperatures.

2.9 Refinement and discussion

The refinement of the high-kalsilite was performed using the atomic parameters listed in Table 2-9. Six cycles of full-matrix least-squares calculation reduced the R-value down to 0.095. The final atomic parameters and interatomic distances are listed in Tables 2-12 and 2-13. The obtained structure of high-kalsilite is almost identical with that confirmed by the high-temperature X-ray powder method (see, Fig. 2-8).

In the high-kalsilite the coordination number of potassium atoms changed to fifteen from nine in the low-form. The electrostatic valence sums were calculated according to the bond-strength – bond-length parameters for M–O bonds, which were propsed by Brown and Shannon (1973) and Brown and Wu (1976). Those values of potassium atom are $s_0 = 0.125$, $R_0 = 2.823$ and $N = 4.7$ and the electrostatic valence sum $(\sum S)$ of potassium was calculated using the following equation:

$$\sum S = \sum S_0 (R/R_0)^{-N}$$
$$= 0.125 \times [6 \times (3.50/2.823)^{-4.7}$$
$$+6 \times (3.33/2.823)^{-4.7}$$
$$+3 \times (2.72/2.823)^{-4.7}]$$
$$= 1.06.$$

The value is almost equivalent to the ideal value (1.0) of K^+.

According to the interatomic distances of Si–O and Al–O listed in Table 2-13, the distribution of silicon and aluminum atoms were ordered. Therefore the space group was determined to be $P6_3mc$. However, the interatomic distances of Si–O(2) and Al–O(2) in high-kalsilite are found to be closer than those in low-kalsilite listed in Table 2-8. Such relation is found also in nepheline structure (Foreman and Peacor, 1970). These values of interatomic distances are close to the ideal values between Si–O (1.604 Å) and Al–O (1.760 Å) (Jones,1968). The fact suggests that some parts of domains may be changed into disordered forms. It would be remained to be solved whether the perfect disordered high-kalsilite with $P6_3/mmc$ symmetry exists or not.

Fig. 2-10 shows the variation of a, c and V values with increasing temperatures. As are obvious in the figure, the variation curves shows two break points at about 650°C and 850°C, respectively. The latter can be corresponded to the inversion point, while the cause of the former remains to be solved. It should be noted that increasing of the a-axis with increasing temperature is caused by thermal expansion. On the other hand, the expansion of the c-axis ceased at 650°C and the c-axis contracts gradually above this temperature. This may be caused by the thermal motion of O(2) atoms linking the framework along the c-axis.

In order to examine the structural characteristics of constituent atoms of high-kalsilite, the Fourier sections parallel to (001) were calculated. The results are shown in Fig. 2-11. As shown in the figure, the contours of the electron density of O(1) atoms are elongated in the direction perpendicular to the T–O–T bonds. In fact, the value of B_{eq} of O(1) atoms is 15.1 and the value corresponds to the very large amplitude of thermal vibration of O(1) atoms along this direction. An-

other oxygen atoms O(2) occupies the off-axial position as in the case of the low-form structure, but the degree of displacement from the ideal threefold position is larger at high temperatures than at low temperatures. This displacement of O(2) atoms probably causes the contraction of the c-axis, as shown in Fig. 2-10.

Fig. 2-12 shows NW-diagram to emphasize group-subgroup relation (Neubueser and Wondratschek, 1966) of kalsilite structures. As shown in the figure, $P6_3$ (low-kalsilite), $P6_3mc$ (high-kalsilite) and $P6_3/mmc$ (disorderedhigh-kalsilite) are in the relation found in Zellengreichen subgroups. The number of equivalent positions are doubled, when the transition occurs from one state to the other. On the other hand, Gottardi(1979) divided the symmetry of framework silicates into three kinds: topologic symmetry(TS): $P6_3/mmc$, topochemical symmetry (TCS): $P6_3mc$ and real symmetry (RS): $P6_3$. This classification of Gottardi corresponds eactly to those of the three types of modification of kalsilite established in the present paper.

3 Kaliophilite

3.1 Research history

In addition to kalsilite, five structural modifications of $KAlSiO_4$ have been reported by some workers as will be described in the following. Those are natural kaliophilite, synthetic kaliophilite, and two types of orthorhombic $KAlSiO_4$.

Natural kaliophilite is an extremely rare mineral and symbolized as kaliophilite-H1 by Merlino (1984). In natural kaliophilites two types of crystal structure are known. Bannister (1931) studied the first type by means of X-ray methods together with chemical and optical examinations and discussed in relation to nepheline structure. Kaliophilite has hexagonal symmetry like in the case of nepheline with symmetry planes, but
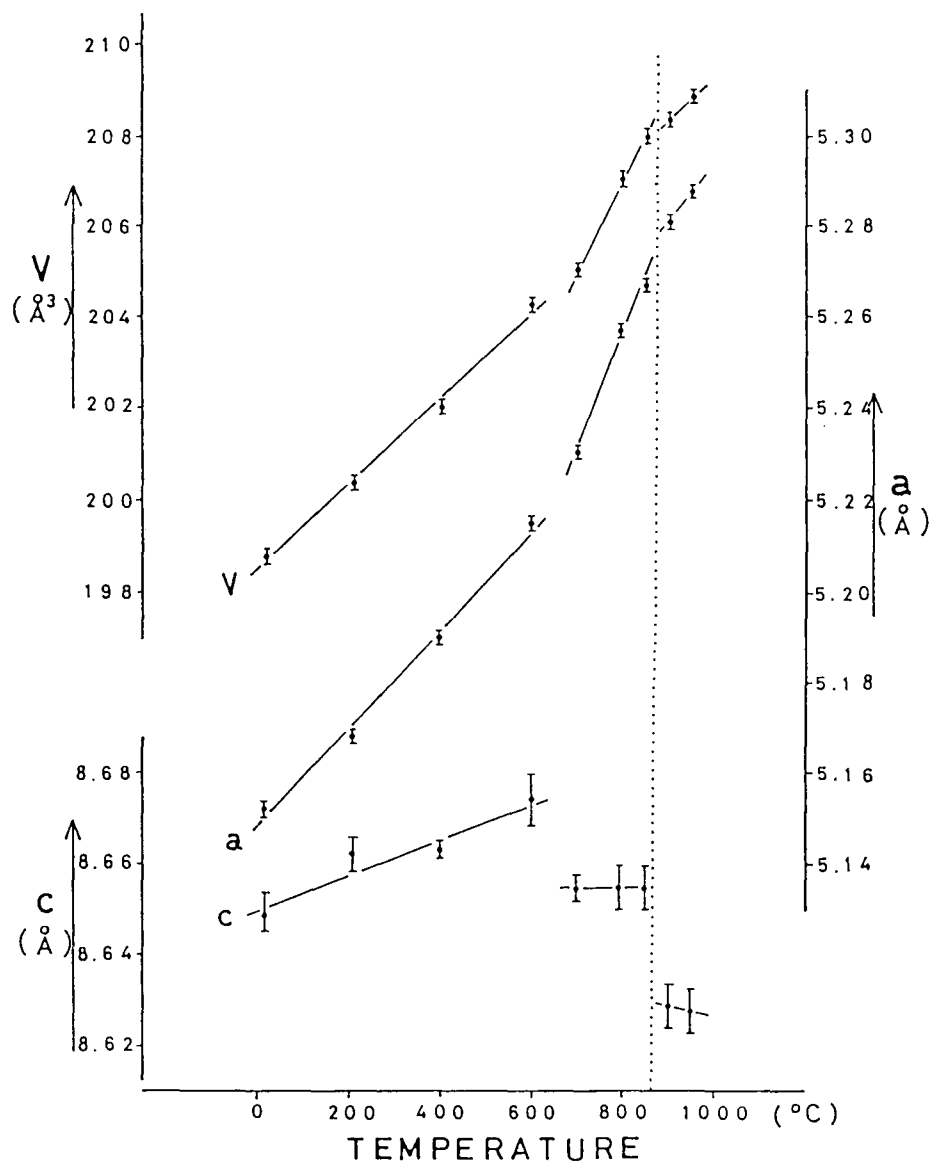
Fig.2-10: Cell dimensions a, c, and V as a function of temperature. Dotted line indicates the inversion point.
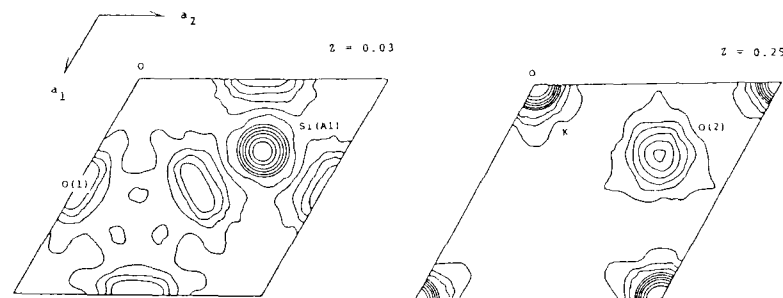

Fig.2-11: Fourier section map (xy) of the structure of high-kalsilite onto (001) plane. Upper, z=0.03. Lower, z=0.25. Contours are at intervals of 1.2 e.Å^{-3} starting from 0.5 e.Å^{-3}.

P6₃/mmc — | High-disorder-kalsilite |
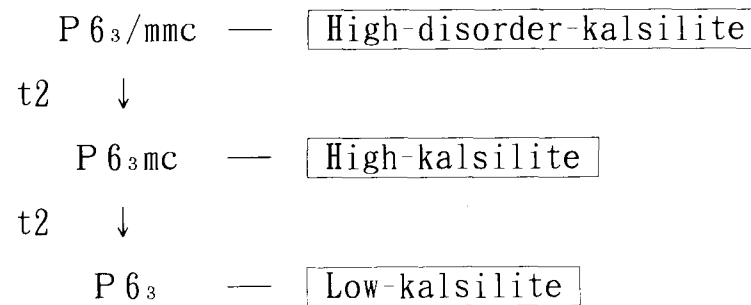
t2 ↓

P6₃mc — | High-kalsilite |

t2 ↓

P6₃ — | Low-kalsilite |

Fig.2-12: The NW-diagram of kalsilite structures.

the unit cell of kaliophilite ($a = 27.0$, $c = 8.6$ Å) is much larger than that of nepheline ($a = 10.4$, $c = 8.5$ Å). The comparison of a-axis of the both minerals indicates that the larger unit cell and symmetry planes of kaliophilite could be explained by a three fold twinning or parallel growth of the nepheline cell. Furthermore, the occupancy of the large potassium atoms in the hole of this structure might produce the distortion enough to build up the larger cell keeping c-axis constant.

Lukesh and Buerger (1942) reported the crystallographic data of natural kaliophilite ($a = 26.94$, $c = 8.55$ Å, space group $P6_322$). Claringsbull and Bannister (1948) suggested that the crystal structure of kaliophilite is probably a multiple kalsilite structure and that the c-axis value is less for kaliophilite than for kalsilite indicated silight flexing of the linkage along the c-axis.

The second type of natural kaliophilite shows anomalous X-ray reflections(Smith and Tuttle, 1957), and it is considered to be the disorder type of natural kaliophilite structure. The anomalous natural kaliophilite has diffuse reflections with $k = 3n$ (n=integers), while the normal natural kaliophilite has sharp ones. Both the normal and the anomalous natural kaliophilite are discovered only in volcanic rocks.

Thugutt (1937) reported on the structure of synthesized kaliophilite but it is not certain whether the sturcute is the same to that of natural kaliophilite(kaliophilite-H1) or not. This is because he did not give X-ray data in his paper. Since Thugutt (1937), kaliophilite-H1 phase has not been synthesized.

Rigby and Richardson (1947) obtained a new phase of $KAlSiO_4$ at temperature of 900°C. The material showed hexagonal symmetry and gave a powder pattern similar to that of kaliophilite-H1. Smith and Tuttle (1957, 1958) synthesized the same phase under hydrothermal conditions ($1,000 \sim 1,100$°C at 500kg/cm² water vapor pres-

sure) and indexed the obtained X-ray powder pattern of the new phase on the basis of the unit cell of kaliophilite-H1. They suggested that this synthetic material might be a disordered form of kaliophilite-H1. They called the phase as 'synthetic kaliophilite'. Later, Merlino (1984) symbolized this synthetic kaliophilite as kaliophilite-H2.

Rigby and Richardson (1947) was successful in producing the orthorhombic $KAlSiO_4$ at temperature above 1,000°C. They also found this orthorhombic phase in blust-furnace linings. They reported that some crystals of them were optically biaxial positive and exhibited aragonite-like twinning or polysynthetic twinning.

Kunze (1954) reported the crystallographic data ($a = 9.013$, $b = 15.673$, $c = 8.574$ Å, space group $P222_1$) and indexed the X-ray powder pattern of the orthorhombic $KAlSiO_4$. He reported that the orthorhombic $KAlSiO_4$ was high temperature polymorph of kaliophilite and that kaliophilite inverted to the orthorhombic form above 1,540°C.

Smith and Tuttle (1957, 1958) synthesized the orthorhombic $KAlSiO_4$ ($a = 9.06$, $b = 15.69$, $c = 8.562$ Å) at temperatures over 840°C. At this temperature kalsilite was considered to change readily to the orthorhombic $KAlSiO_4$ and the transition was reversible under hydrothermal conditions. The orthorhombic $KAlSiO_4$ demonstrated the pseudo-hexagonal nature and the powder pattern could be indexed on the basis of hexagonal geometry. Smith and Tuttle called this orthorhombic phase O1 and Merlino (1984) symbolized this phase as kaliophilite-O1.

Cook, Roth, Parker, and Negas (1977) studied the $KAlSiO_4$-$KAlO_2$ join in the system K_2O-Al_2O_3-SiO_2. They reported that the orthorhombic $KAlSiO_4$ (kaliophilite-O1) can be synthesized at 950°C ($a = 9.057(2)$, $b = 15.642(2)$, $c = 8.582(2)$ Å, space group $P2_122_1$) and that this phase transforms into another high-temperature orthorhombic phase above $1,450 \sim 1,485$°C

(a18.110(3), b = 15.600(3), c = 8.560(2) Å, space group $P2_1am$, $Pma2$ or $Pmam$).

In Table 3-1, structural data of natural and synthetic polymorphs of KAlSiO$_4$ are summarized. As mentioned above, structural relation of kaliophilite and kalsilite was proposed. However, no structual model can explain reasonably the powder patterns of both exact intensities and positions. In this report, therefore, kaliophilite was synthesized and the structure of the obtained crystals was first investigated by the X-ray powder method.

3.2 Synthesis of kaliophilite

Kaliophilite was synthesized by the dry method. Starting materials used in the present experiments are mixture of special grade reagents of activated alumina (Al$_2$O$_3$), silica gels (SiO$_2$), and K$_2$CO$_3$. These starting materials were put in the porcelain boat and heated in the electric fireplace at the temperature range from 800° to 1,250°C, and quenched after holding at cretain temperature for 2 hours. The starting materials, heating temperature and the main products are shown in Table 3-2.

Two kinds of crystalline phases were obtained through this syntheses. One is kaliophilite and another is orthorhombic phase. However, crystals appropriate for single crystal analysis were not obtained. The two phases showed the same X-ray powder pattern to those reported by Smith and Tuttle (1957). The obtained kaliophilite is not kaliophilite-H1 but kaliophilite-H2, and the other orthorhombic phase is kaliophilite-O1.

Kaliophilite-H2 was produced at lower temperature from the mixture containing higher contents of aluminum. while kaliophilite-O1 was produced at higher temperature.

The values of cell dimensions of these phases were calculated based on the obtained X-ray powder data using CuKα radiation. The obtained re-

sults are given in Table 3-3 and Table 3-4, respectively. In the measurements, silicon was used as an internal standard. The cell dimensions were refined using the program RSLC3 of UNICS (Sakurai, 1971). The values of kaliophilite-H2 are a = 5.17(1), c = 8.49(3) Å, and those of kaliophilite-O1 are a = 9.01(1), b = 15.60(2), c = 8.53(4) Å. These nalues are close to those of the previous results, respectively.

3.3 Examination of the structure

Kaliophilite-H2 was considered to be a disordered form of kaliophilite-H1 (Smith and Tuttle, 1957, 1958). However, the a-axis of kaliophilite-H2 (5.17 Å) is much smaller than that of kaliophilite-H1 (26.9 Å), and is close to that of kalsilite (5.15 Å). Also the c-axis of kaliophilite-H2 (8.49 Å) has a near value of that of kalsilite (8.69 Å). Therefore kaliophilite-H2 is probably a disordered form of kalsilite rather than that of kaliophilite-H1 (Okamoto and Kawahara, 1996).

Fig. 3-1 shows four possible types of the unit cell of the kalsilite structure. Types (a) and (b), or types (c) and (d) have the mirror-equivalent positions respectively. Types (a) and (d), or types (b) and (c) are the quite identical structure and have relations in translation by a half period to the c-axis. The geometorical relationship of these four domains can be explained as twinning by merohedory (Friedel, 1926).

In the synthetic kalsilite obtained in this investigation or the alkali-exchanged kalsilite reported by Dollase and Freeborn (1977), Types (a) and (b), or types (c) and (d) have relations to form the domain structures and X-rays diffract coherently by the domains. Considering this fact, if kaliophilite-H2 is a disordered form of kalsilite and the crystal structure is composed of four domains (types (a), (b), (c) and (d)), X-rays can diffract coherently by these four domains. In this case, the calculation of structure factors can be carried out on the

Table 3-1: Natural and synthetic phases with composition of $KAlSiO_4$.

Phase	Composition	Symmetry	a [Å]	b [Å]	c [Å]	references
high-kalsilite(950°C)	$KAlSiO_4$	$P6_3mc$	5.288		8.628	a
kalsilite	$KAlSiO_4$	$P6_3$	5.161		8.699	b
trikalsilite	$Na_{0.3}K_{0.7}AlSiO_4$	hexagonal	15.4		8.6	c
tetrakalsilite	$Na_{0.3}K_{0.7}AlSiO_4$	hexagonal	20.46		8.534	d
orthorombic $KAlSiO_4$-O1	$KAlSiO_4$	$P2_122_1$	9.057	15.642	8.582	e
high-orthorombic $KAlSiO_4$	$KAlSiO_4$	$P2_1am$	18.110	15.600	8.560	e
orthorombic $KAlSiO_4$-O2	$Na_{0.2}K_{0.8}AlSiO_4$	orthorombic	8.892	10.468	8.547	d
natural kaliophilite-H1	$KAlSiO_4$	$P6_322$	26.94		8.55	f
synthetic kaliophilite-H2	$KAlSiO_4$	hexagonal	5.18		8.559	d

references   a : in this report   b : Perrota & Smith(1965)

c : Sahama & Smith(1957)   d : Smith & Tuttle(1957)

e : Cook, Roth, Parker & Negas(1977)   f : Lukesh & Buerger(1942)

Table 3-2: Experimental conditions of kaliophilite-H2 and -O1 synthesis.

Starting materials Al_2O_3 : SiO_2 : K_2CO_3	Heating temperature[°C]	Product
1.0 : 0.8 : 1.5	800	Gl
1.0 : 0.8 : 1.5	900	Gl
1.0 : 0.8 : 1.5	1,000	Gl
1.0 : 0.8 : 1.5	1,100	H2
1.0 : 0.8 : 1.5	1,200	H2
1.0 : 0.8 : 1.5	1,250	H2
1.0 : 0.9 : 1.5	800	Gl
1.0 : 0.9 : 1.5	900	Gl
1.0 : 0.9 : 1.5	1,000	Gl
1.0 : 0.9 : 1.5	1,100	H2
1.0 : 0.9 : 1.5	1,200	H2
1.0 : 0.9 : 1.5	1,250	H2
1.0 : 1.0 : 1.5	800	Gl
1.0 : 1.0 : 1.5	900	Gl
1.0 : 1.0 : 1.5	1,000	H2
1.0 : 1.0 : 1.5	1,100	H2
1.0 : 1.0 : 1.5	1,200	O1
1.0 : 1.0 : 1.5	1,250	O1
1.0 : 1.1 : 1.5	800	Gl
1.0 : 1.1 : 1.5	900	H2
1.0 : 1.1 : 1.5	1,000	O1
1.0 : 1.1 : 1.5	1,100	H2
1.0 : 1.1 : 1.5	1,200	O1
1.0 : 1.1 : 1.5	1,250	O1
1.0 : 1.2 : 1.5	800	Gl
1.0 : 1.2 : 1.5	900	Gl
1.0 : 1.2 : 1.5	1,000	H2
1.0 : 1.2 : 1.5	1,100	H2
1.0 : 1.2 : 1.5	1,200	O1
1.0 : 1.2 : 1.5	1,250	O1
1.0 : 1.3 : 1.5	800	Gl
1.0 : 1.3 : 1.5	900	H2
1.0 : 1.3 : 1.5	1,000	H2
1.0 : 1.3 : 1.5	1,100	O1
1.0 : 1.3 : 1.5	1,200	O1
1.0 : 1.3 : 1.5	1,250	O1
1.0 : 1.4 : 1.5	800	Gl
1.0 : 1.4 : 1.5	900	H2
1.0 : 1.4 : 1.5	1,000	H2
1.0 : 1.4 : 1.5	1,100	O1
1.0 : 1.4 : 1.5	1,200	O1
1.0 : 1.4 : 1.5	1,250	O1
1.0 : 1.5 : 1.5	800	Gl
1.0 : 1.5 : 1.5	900	H2
1.0 : 1.5 : 1.5	1,000	O1
1.0 : 1.5 : 1.5	1,100	O1
1.0 : 1.5 : 1.5	1,200	O1
1.0 : 1.5 : 1.5	1,250	O1
1.0 : 1.6 : 1.5	800	Gl
1.0 : 1.6 : 1.5	900	H2
1.0 : 1.6 : 1.5	1,000	O1
1.0 : 1.6 : 1.5	1,100	O1
1.0 : 1.6 : 1.5	1,200	O1
1.0 : 1.6 : 1.5	1,250	O1
1.0 : 1.7 : 1.5	800	Gl
1.0 : 1.7 : 1.5	900	Gl
1.0 : 1.7 : 1.5	1,000	O1
1.0 : 1.7 : 1.5	1,100	O1
1.0 : 1.7 : 1.5	1,200	O1
1.0 : 1.7 : 1.5	1,250	O1
1.0 : 1.8 : 1.5	800	Gl
1.0 : 1.8 : 1.5	900	Gl
1.0 : 1.8 : 1.5	1,000	Gl
1.0 : 1.8 : 1.5	1,100	O1
1.0 : 1.8 : 1.5	1,200	O1
1.0 : 1.8 : 1.5	1,250	O1
1.0 : 1.9 : 1.5	800	Gl
1.0 : 1.9 : 1.5	900	Gl
1.0 : 1.9 : 1.5	1,000	Gl
1.0 : 1.9 : 1.5	1,100	O1
1.0 : 1.9 : 1.5	1,200	O1
1.0 : 1.9 : 1.5	1,250	O1
1.0 : 2.0 : 1.5	800	Gl
1.0 : 2.0 : 1.5	900	Gl
1.0 : 2.0 : 1.5	1,000	Gl
1.0 : 2.0 : 1.5	1,100	Gl
1.0 : 2.0 : 1.5	1,200	O1
1.0 : 2.0 : 1.5	1,250	O1
1.0 : 2.1 : 1.5	800	Gl
1.0 : 2.1 : 1.5	900	Gl
1.0 : 2.1 : 1.5	1,000	Gl
1.0 : 2.1 : 1.5	1,100	Gl
1.0 : 2.1 : 1.5	1,200	O1
1.0 : 2.1 : 1.5	1,250	O1
1.0 : 2.2 : 1.5	800	Gl
1.0 : 2.2 : 1.5	900	Gl
1.0 : 2.2 : 1.5	1,000	Gl
1.0 : 2.2 : 1.5	1,100	Gl
1.0 : 2.2 : 1.5	1,200	Gl
1.0 : 2.2 : 1.5	1,250	O1

Product   H2 : kaliophilite-H2 (synthetic kaliophilite)

O1 : kaliophilite-O1 (orthorhombic $KAlSiO_4$)

Gl : glass

Table 3–3: The X–ray powder data of kaliophilite-H2.

d(obs.) [Å]	I(obs.)	h k l	d(calc.) [Å]
4.507	8	1 0 0	4.481
4.271	20	0 0 2	4.245
3.082	100	1 0 2	3.081
2.572	41	1 1 0	2.587
2.186	11	1 1 2	2.209
2.096	12	0 0 4	2.122
1.518	7	2 1 2	1.573

Table 3–4: The X–ray powder data of kaliophilite-O1.

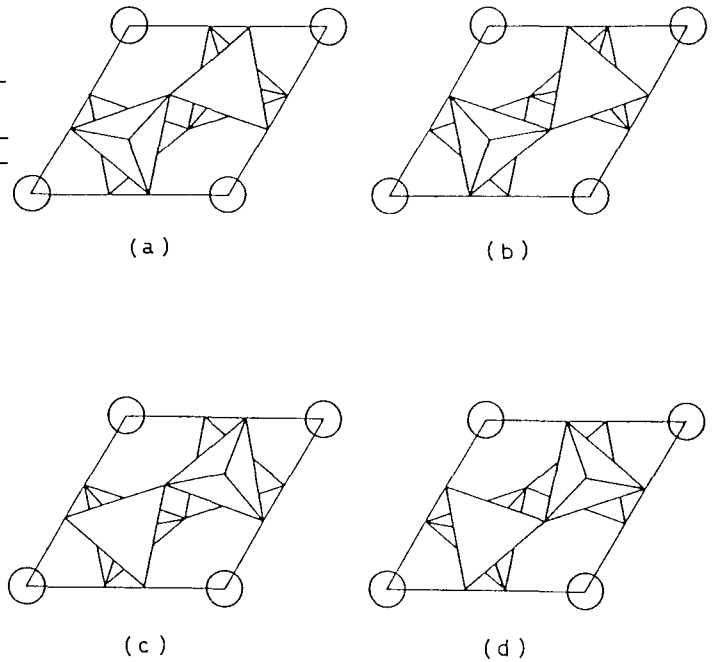| d(obs.) [Å]	I(obs.)	h k l	d(calc.) [Å]
5.799	7	0 2 1	5.758
		1 1 1	
4.521	9	2 0 0	4.504
		1 3 0	
4.267	13	0 0 2	4.267
3.990	6	2 0 1	3.983
		1 3 1	
3.860	12	2 1 1	3.859
3.541	28	2 2 1	3.548
		0 4 1	
3.400	29	2 3 0	3.405
3.291	7	1 4 1	3.301
3.152	8	2 3 1	3.162
3.082	100	1 3 2	3.098
		2 0 2	
2.934	8	2 4 0	2.949
		3 1 0	
2.770	37	2 4 1	2.787
		3 1 1	
3.644	13	0 2 3	2.637
		1 1 3	
2.578	74	3 3 0	2.600
		0 6 0	
2.221	8	2 6 0	2.252
		4 0 0	
2.188	16	3 3 2	2.221
		0 6 2	
2.094	12	0 0 4	2.134
2.062	6	4 2 1	2.134
		3 5 1	
2.028	11	4 3 0	2.067

(a)　　　(b)

(c)　　　(d)

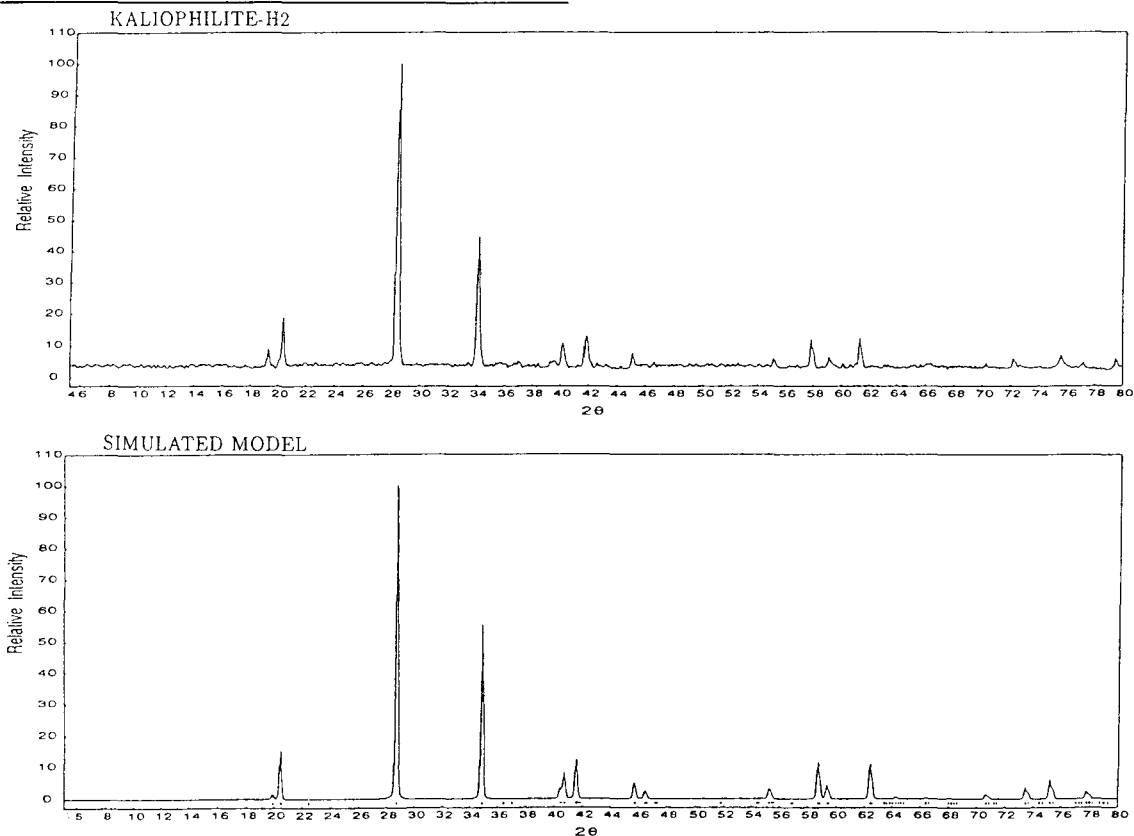Fig.3–1: Four types of the unit cell of the kalsilite structure.

Fig.3–2: X-ray powder patterns of kaliophilite-H2 and its simulated model.

assumption that an unit cell of kaliophilite-H2 is based on the model constructed by the overlap of the four unit cells (types **(a)**, **(b)**, **(c)** and **(d)**). The powder pattern calculated by the program (PPDP) was compared with that observed for the present phase. The result is illustrated in Fig. 3-2. The powder pattern of the simulated model is almost perfectly agreed with that of kaliophilite-H2.

3.4　Refinement and discussion

The refinement of kaliophilite-H2 was carried out using the method introduced by Rietveld (1969) and calculated by RIETAN (Izumi, 1993). The positional parameters used were those of synthetic kalsilite (see, Table 2 7) and the space group was $P6_3mc$. Scattering factors corresponding to neutral atoms were used throughout the calculations (International Tables for X-ray Crystallography, 1974).
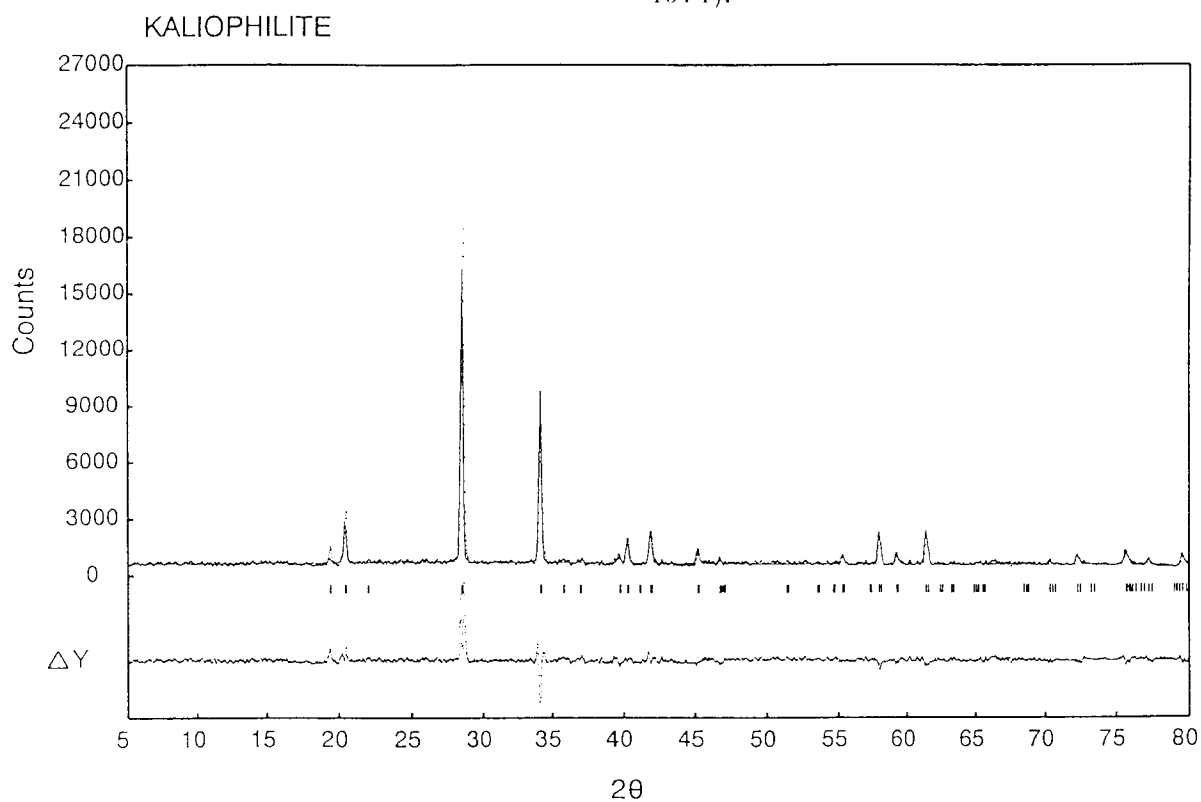

Fig.3-3: Pattern fitting between observed and calculated one for kaliophilite-H2.

Table 3-5: Atomic parameters of kaliophilite-H2.

Atom	multiplicity	x	y	z	$B_{eq.}$
K(1)	1.0	0	0	0.25	1.86(5)
K(2)	1.0	0	0	0.75	1.86(5)
Al(1)	1.0	1/3	2/3	0.054(2)	1.84(12)
Al(2)	1.0	1/3	2/3	0.554(2)	1.84(12)
Si(1)	1.0	1/3	2/3	0.434(1)	1.19(9)
Si(2)	1.0	1/3	2/3	0.934(1)	1.19(9)
O(1)	1.5	0.391(2)	0.986(2)	0.489(2)	2.69(20)
O(2)	1.5	0.391(2)	0.986(2)	0.989(2)	2.69(20)
O(3)	1.0	0.358(8)	0.641(4)	0.252(6)	2.99(30)
O(4)	1.0	0.358(8)	0.641(4)	0.752(6)	2.99(30)

After nine cycles of the least squares refinement, the structure of kaliophilite-H2 was converged to the final R-value of 0.121 for isotropic temperature factors, giving equal weights to all reflections. The final positional parameters and isotropic temperature factors are shown in Table 3-5. The pattern fitting obtained between observed and calculated one is shown in Fig. 3-3. The rather high R-value may be due to the random arrangement of the domain structure.

As shown in Table 3-2, kaliophilite-H2 was produced from the starting materials containing excess aluminum more than equivalent contents of aluminum and silicon (Si : Al = 1 : 1). Excess aluminum atoms may play certain role for the construction of the domain structure and probably be concentrated near the domain boundaries. Therefore, the violation of the Al-O-Al avoidance rule (Loewnstein, 1954) can possibly act along the boundaries of the four different domains.

As mentioned above, kaliophilite-H2 is considered to be a disordered form of domain structures of kalsilite. If single crystals of kaliophilite-H2 can be obtained and if a single crystal analysis will be carried out, cell dimensions, atomic parameters, temperature factors and occupation factors will be refined more accurately. Establishment of the detailed structure of kaliophilite-H2 will give significant information in order to presume the unknown structure of such minerals as kaliophilite-H1 and kaliophilite-O1 in the system of NaAlSiO$_4$-KAlSiO$_4$.

4   Summary

Single crystals of kalsilite were synthesized and structural refinement was carried out to explain the structural details of the pure end-member of NaAlSiO$_4$-KAlSiO$_4$ series. 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 obtained structure agrees with those of the natural kalsilite (Perrota and Smith, 1965). Moreover, synthetic kalsilite has the same domain structure to that of alkali-exchanged kalsilite reported previously(Dollase and Freeborn, 1977). The oxygen atoms, O(1), which link tetrahedral atoms forming ditrigonal rings, are disordered at two mirror-equivalent sites. The site occupancy ratio of O(1) atoms between these two positions were also refined on the assumption of the existence of domain structures whose arrangement is rather random resulting coherent diffraction of X-rays. The final R-value is 0.084 for 373 observed reflections. The alkali-exchanged kalsilite, on the other hand, gives diffuse streaks parallel to the c^* direction corresponding to the structural disorder in the stacking on the (001) plane, but the synthetic kalsilite gives sharp diffraction spots along the c^* direction. The volume ratios 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.

The domain structure of the synthetic kalsilite was considered to be due to the high–low inversion, and the structural model of the high-form was constructed. The heating experiments revealed that the X-ray powder pattern changed at 865°C. At this temperature kalsilite underwent a dispalcive transition like quarz or tridymite.

The extinction of hhl, l–odd reflection at 865°C suggests that the space group of kalsilite changes from $P6_3$ of the low-form to $P6_3mc$ of the high-form. In order to confirm this structural change, the single crystal structure analysis at 950°C was carried out with an automated four-circle diffractometer equipped with an electric furnance. As a result, it was confirmed that kalsilite underwent a displacive transition at 865°C.

The high-kalsilite is hexagonal and the space group is $P6_3mc$, with $a = 5.288(1)$ and $c = 8.628(5)$ Å at 950°C. Large thermal vibration of O(1) atoms is observed along the direction perpendicular to the bonding of O(1) and Si(Al) atoms. Based on the bond distances between Si(Al)-O(1) atoms, the structure is considered to be partly changed into disordered kalsilite whose space group is $P6_3/mmc$. The space group of the low-kalsilite is $P6_3$, and the high-form is considered to be divided into two groups, high-kalsilite ($P6_3mc$) and disordered high-kalsilite ($P6_3/mmc$). The Zellengleichen subgroup relations are found among these three polymorphs.

The syntheses of kaliophilite have been carried out from the starting materials of near kalsilite compositions ($KAlSiO_4$), of which the Al_2O_3/SiO_2 ratio is greater than $1/2$. The X-ray powder diffraction pattern fits well to those of previous investigators. The crystal structure of the obtained kaliophilite-H2 is proposed by using the model consisted of four different types of kalsilite structure. In order to confirm this hypothesis, the analysis was carried out by means of Rietvelt method. The positions and intensities of the X-ray powder diffractions can be explained on the basis of these four domains, belonging to the twinning by merohedory. As a result of the conditions of the syntheses, it may be supposed that the violation of the Al–O–Al avoidance rule can possibly act along the domain boundaries.

In conclusion, three $KAlSiO_4$ minerals (kalsilite, kaliophilite-H2 and kaliophilite-O1) were synthesized successfully in this investigation. It has been clarified that kalsilite undergoes a displacive transition to change to high-kalsilite, and that low-kalsilite has domain structure. Kaliophilite-H2 is constructed of those domain structures and the structure of kalsilite is the most fundamental structure of these minerals. Although some structures in the Ne-Ks series remain to be solved,

the structural characteristics of $KAlSiO_4$ minerals established in this report contribute greatly to further research on crystal structures as well as phase relations of Ne–Ks series in the feldspathoid groups.

Acknowledgments

References

Andou,Y. & Kawahara,A. (1982). The existence of high-low inversion point of kalsilite. Mineral. Jour., 11, 2, 72–77.

Andou,Y. & Kawahara,A. (1984). The refinement of the structure of synthetic kalsilite. Mineral. Jour., 12, 4, 153–161.

Bannister,F.A. (1931). A chemical, optical and X-ray study of nepheline and kaliophilite. Mineral. Mag., 22, 569–608.

Bannister,F.A. & Hey,M.H. (1942). Kalsilite, a polymorph of $KAlSiO_4$, from Uganda. Mineral. Mag., 26, 218–224.

Bannister,F.A., Sahama,Th.G. & Wiik,H.B. (1952). Kalsilite in venanzite from San Venanzo, umbrica, Italy. Mineral. Mag., 30, 46–48.

Bradley,A.J. (1925). The crystal structure of lithium potassium sulphate.Phil. Mag., 49, 1225–1237.

Brown,I.D. & Shannon,R.D. (1973). Empirical bond strength bond length curves for oxides. Acta Cryst., A29, 266–282.

Brown,I.D. & Wu,K.K. (1976). Empirical parameters for calculating cation–oxygen bond valences. Acta Cryst., B32, 1957–1959.

Buerger,M.J. (1954). The stuffed derivatives of the silica structure. Amer. Mineral., 39, 600–614.

Buerger,M.J., Klein, G.E. & Donnay,G. (1954). Determination of the crystal structure of nepheline. Amer. Mineral., 39, 805–818.

Claringsbull,G.F. & Bannister,F.A. (1948). The crystal structure of kalsilite. Acta Cryst., 1, 42–43.

Cohen,L.H. & Klement,W.Jr. (1976). Effect of pressure on reversible solid–solid transition in nepheline and carnegieite. Mineral. Mag., 40, 487–492.

Cook,L.P., Roth,R.S., Parker,H.S. & Negas,T. (1977). The system K₂O–Al₂O₃–SiO₂. Part I. Phase on the KAlSiO₄ KAlO₂ join. Amer. Mineral., 62. 1180 1190.

Dollase,W.A. (1970). Least-squares refinement of the structure of a plutonic nephline. Zeit. Krist., 132, 27 44.

Dollase,W.A. & Peacor,D.R. (1971). Si Al ordering in nephelines. Contrib. Mineral. Petrol., 30, 129 134.

Dollase,W.A. & Freeborn,W.P. (1977). The structure of KAlSiO₄ with P6₃mc symmetry. Amer. Mineral., 62, 336–340.

Dollase,W.A. &Thomas. W.M. (1978). The crystal chemistry of silica-rich alkali-deficient nepheline. Contrib. Mineral. Petro., 66, 311–318.

Foreman,N. & Peacor.D.R. (1970). Refinement of the nepheline structure at several temperatures. Zeit. Krist., 132, 45 70.

Friedel,G. (1926). Leçons de Cristallographie. Berger–Levrault, Paris.

Gottardi,G. (1979). Topologic symmetry and real symmetry in framework silicates. Tschermaks Min. Petr. Mitt., 26, 39 50.

Gregorkiewitz,M. (1980). Synthese und Charakterisierung poröser Silikate, Dissertation der Technischen Hochschule Darmstadt.

Hahn,T. & Buerger,M.J. (1955). The detailed structure of nepheline, KNa₃Al₄Si₄O₁₆. Zeit. Krist., 106, 308 338.

Henderson,C.M.B. & Roux,J. (1977). Inversions in subpotassic nephelines. Contrib. Mineral. Petrol., 61, 279–298.

Henderson,C.M.B. & Thompson,A.B. (1980). The low-temperature inversion in subpotassic nepheline. Amer. Mineral., 65, 970–980.

Holmes,A. (1942). A suite of volcanic rocks from south-west Uganda containing kalsilite (a polymorph of KAlSiO₄) Mineral. Mag., 26, 197–217.

International Tables for X-ray Crystallography (1974). Vol.1,2,3.

Izumi,F. (1993). The Rietvelt Method (ed. by Young,R.A.), Oxford Univ. Press, Chap. 13.

Jay,A.H. & Andrews,K.W. (1947). X-ray reflections of kalsilite (K₂O·Al₂O₃·2SiO₂). Mineral. Mag., 28, 88 89.

Jones,J.B. (1968). Al-O and Si O tetrahedral distances in alumino-silicate framework structures. Acta Cryst., B 24, 355 35

Kawahara,A. , Andou,Y. , Marumo,F. & Okuno,M. (1987). The crystal structure of high temperature form of kalsilite(KAlSiO₄) at 950°C. Mineral. Jour., 13, 5, 260 270.

Kunze,G. (1954). Ueber die rhombische modificationen von KAlSiO₄ in Anlehnung an den Kalsilit. Heidelberger Beitr. zur Min. und Petro., 4, 99 129.

Loewenstein,W. (1954). The distribution of aluminum in the tetrahedra of silicates and aluminates. Amer. Mineral., 39, 92 96.

Lukesh,J.S. & Buerger,M.J. (1942). The unit cell and space group of kaliophilite. Amer. Mineral., 27, 226–227.

Luth,W.C. & Tuttle,O.F. (1963). Externally heated cold-seal pressure vessels for use to 10,000 bars and 750°C. Amer. Mineral., 48. 1401–1403.

McConnel,J.D.C. (1962). Electron-diffraction study of subsidiary maxima scattered intensity in nepheline. Mineral. Mag., 33, 114 124.

McConnel,J.D.C. (1981). Time–Temperature study of the intensity of satellite reflections in nepheline. Amer. Mineral., 66, 990 996.

Merlino,S. (1984). Feldspathoids : their average and real strucutes. Feldspars and Feldspathoids (ed. by Brown,W.L.), D. Reidel Publishing Company, 435 470.

Neubüser,J. & Wondratschek,H. (1966). Technik, 1, 529–543.

Nukui,A & Nakazawa,H (1980). Polymorphism in tridymite. Min. Jour., 14, 364–386.

Okamoto,Y. and Kawahara,A. (1996). Interpretation of the crystal structure of synthetic kaliophilite from the domain structure of kalsilite. Okayama Univ. Earth Science Reports, 3, 1, 57–64.

Parker,J.M. (1972). The domain structure of nepheline. Zeit. Krist., B6, 255–272.

Perrota,A.J. & Smith,J.V. (1965). The crystal structure of kalsilite, KAlSiO₄, Mineral. Mag., 35, 588–595.

Rigby,G.R. & Richardson,H.M. (1947). The occurrence of artificial kalsilite and allied potassium aluminum silicates in blast furnace linings. Mineral. Mag., 28, 75–88.

Ribbe,P.H. (1984). Average structures of alkali and plagioclase feldspars : systematics and applications. Feldspars and Feldspathoids (ed. by Brown,W.L.), D. Reidel Publishing Company, 435–470.

Rietvelt,H.M. (1969). Journ. Appl. Cryst., 10, 7–11.

Sahama,Th.G. (1958). A complex form of natural nepheline from Iivaara, Finland. Amer. Mineral., 43, 165 166.

Sahama,Th.G. (1960). Kalsilite in the lavas of Mt. Nyiragongo (Belgian Congo). Jour. Petrol., 1, Part 2, 146–171.

Sahama,Th.G. (1962). Order disorder in natural nepheline solid solution. Jour. Petrol., 3, Part 1, 65–81.

Sahama,Th.G. & Smith,J.V. (1957). Trikalsilite, a new mineral. Amer. Mineral. 42, 286.

Sakurai,T. (1971). The Universal Crystallographic Computation Program System. The Crystallographic Society of Japan, Tokyo.

Simmons,W.B. & Peacor,D.R. (1972). Refinement of the crystal structure of a volcanic nepheline. Amer. Mineral., 57, 1711–1719.

Smith,J.V. (1953). Reexamination of the crystal structure of melilite. Amer. Mineral., 38, 643–661.

Smith,J.V. & Sahama,Th.G. (1954). Determination of the composition of natural nepheline by an X-ray method. Mineral. Mag., 30, 439–449.

Smith,J.V. & Sahama,Th.G. (1957). Order-disorder in kalsilite. Amer. Mineral., 42, 287–288.

Smith,J.V. & Tuttle,O.F. (1957). The nepheline–kalsilite system : I. X-ray data for the crystalline phase. Amer. Jour. Sci., 255, 282–305.

Smith,J.V. & Tuttle,O.F. (1958). The nepheline–kalsilite system : II. Phase relations. Amer. Jour. Sci., 256, 571–589.

Thugutt,St.J. (1937). O Syntetycznym kaliojilicie. Arch. Min. Tow. Nauk. Warszawa, 13, 109–111.

Tilley,C.E. (1954). Nepheline–alkali feldspar parageneses. Amer. Jour. Sci., 252, 65–75.