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$KAlSiO_4$ stuffed derivatives of tridymite: phase relationships

RICHARD N. ABBOTT, JR.

Department of Geology
Appalachian State University
Boone, North Carolina 28608

Abstract

In the system $(K,Na)AlSiO_4$, there are several stuffed derivatives of tridymite, the most common of which are nepheline, kalsilite and kaliophilite. The phase relationships, as described by Tuttle and Smith (1958), are unusual in that the density of symmetry elements is higher in the low temperature polymorphs (nepheline and kalsilite) than in the high temperature polymorphs (orthorhombic $KAlSiO_4$, tetrakalsilite and kaliophilite).

The purpose of this study is to reassess the phase relationships for the potassic side of the system in the light of (1) theoretical considerations regarding Al–Si order–disorder and displacive transformations and (2) a new analysis of the diffraction patterns of some of the polymorphs. It is shown that the orthorhombic $KAlSiO_4$ and tetrakalsilite are most likely metastable, produced during quenching. The stable polymorphs have approximately the same unit cell volume as kalsilite and include a hypothetical, Al–Si disordered $P6_3/m2/m2/c$ polymorph above 850°C, a hypothetical, Al–Si ordered $P6_3mc$ polymorph at intermediate temperatures and kalsilite, $P6_3$, at low temperatures. The other polymorphs are unstable relative to one or the other of these depending on the temperature and annealing time. The so-called synthetic kaliophilite reported by Tuttle and Smith (1958) may in fact be either the high temperature $P6_3/m2/m2/c$ polymorph or the intermediate temperature $P6_3mc$ polymorph.

Rotation twins and mirror twins should occur in kalsilite which has transformed from the high temperature, Al–Si disordered $P6_3/m2/m2/c$ polymorph. During cooling Al–Si ordering results in a reduction in symmetry to $P6_3mc$ and this should result in twins related by 2-fold rotation. Natural kaliophilite probably represents a transitional or Ostwald state between $P6_3/m2/m2/c$ and $P6_3mc$. Upon further cooling, displacive transformation of the framework results in another reduction in symmetry to $P6_3$ (kalsilite). This last transformation should cause mirror twins.

Introduction

The phase relationships for the system $NaAlSiO_4$–$KAlSiO_4$, determined by Tuttle and Smith (1958), involve a number of polymorphs which are stuffed derivatives (Buerger, 1947) of tridymite. The polymorphs are characterized in Table 1 and the phase relationships suggested by Tuttle and Smith (1958) are reproduced in Figure 1. The phase relationships for the sodic side of the diagram have been modified according to the experiments of Henderson and Thompson (1980). Carnegieite is the only crystalline phase in Figure 1 which is not a stuffed derivative of tridymite. Carnegieite is, however, a stuffed derivative of cristobalite. Hence, the polymorphic transformation from nepheline to carnegieite is analogous to the polymorphic transformation from tridymite to cristobalite. This paper is devoted to the stuffed derivatives of tridymite. Perhaps the most common of these polymorphs are nepheline, kalsilite and kaliophilite.

The phase relationships proposed by Tuttle and Smith (1958) for the potassic side of the system in Figure 1 are unusual because the low temperature polymorphs, nepheline and kalsilite, have more symmetry than the high temperature polymorphs, H4 and O1. This is manifested in two ways: (1) The high temperature polymorph O1 has a lower order space group than the low temperature kalsilite. (2) The unit cell volumes for the high temperature forms are several times larger than the unit cell volumes for the corresponding low temperature forms. Hence, the density of symmetry elements is lower in the high temperature polymorphs than in the low temperature polymorphs. This contradicts the behavior of other systems including the sodic side of the $(Na,K)AlSiO_4$ system (Henderson and Thompson, 1980) and also contradicts the behavior expected on the basis of the thermodynamics of changes in symmetry accompanying either displacive transformations or order–disorder transformations (Strens, 1967; Burnham, 1973).

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Table 1. Polymorphs of $(K,Na)AlSiO_4$*

Name	Symbol	Wt.% $NaAlSiO_4$	Symmetry	Lattice parameters (A) a	b	c
carnegieite	Cg	90-100	cubic	7.3	--	--
nepheline	Ne	30-100	$P\ 6_3$	10.0	--	8.4
kalsilite	Ks	0-20	$P\ 6_3$	5.2	--	8.7
orthorhombic $KAlSiO_4$	O1	0-10	$P\ 2\ 2\ 2_1$	9.1	15.7	8.56
orthorhombic $KAlSiO_4$	O2	near 20	orthorhombic	8.9	10.5	8.5
trikalsilite	H3	near 30	$P\ 6_3$	15.4	--	8.6
tetrakalsilite	H4	near 30	$P\ 6_3$ ($P\ 6_3\ 2\ 2$)	20.5	--	8.6
natural kaliophilite	Kp	0-10	$P\ 6_3\ 2\ 2$	26.9	--	8.5
synthetic kaliophilite	s-Kp	0-10	hexagonal	5.2	--	8.6

* Smith and Tuttle (1957)
Sahama and Smith (1957) for trikalsilite, H3

The high temperature polymorphs suggested by Tuttle and Smith (1958), O1 and H4 in Figure 1, were identified at room temperature, after quenching from high temperatures. Bowen (1917) reported that the orthorhombic polymorph (O1 of Tuttle and Smith, 1958) occurs as pseudohexagonal crystals with sector twinning or polysynthetic twinning. This suggests transformation from a higher temperature polymorph. The O1 polymorph with polysynthetic twinning can be made by quenching the synthetic kaliophilite from high temperatures (Bowen, 1917).

The purpose of this study is to reassess the phase relationships for the potassic endmember of the system in the light of (1) theoretical considerations regarding Al–Si order–disorder transformations and displacive transformations and (2) a new analysis of the diffraction patterns of kaliophilite and synthetic kaliophilite.

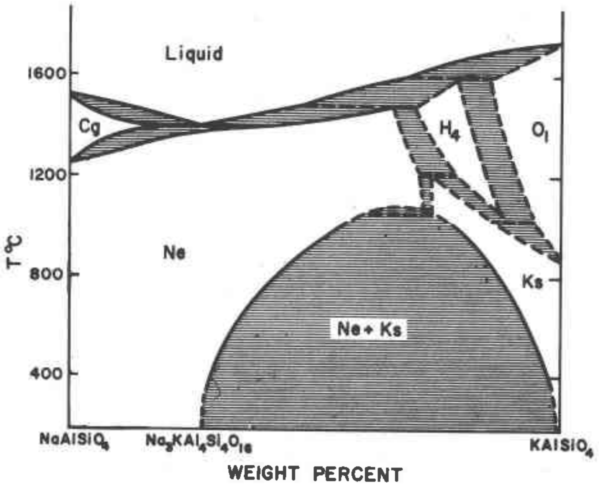

Fig. 1. Phase relationships for the system $NaAlSiO_4$–$KAlSiO_4$ after Tuttle and Smith (1958). The sodic end of the diagram has been modified according to the findings of Henderson and Thompson (1980). The abbreviations for the different polymorphs are explained in Table 1.

Structures of the stuffed derivatives of tridymite

Buerger (1947) introduced the concept of stuffed derivative structures. In the context of this investigation, the structures of the $(Na,K)AlSiO_4$ polymorphs (except carnegieite) can be derived from the structure of high tridymite by substituting Al for half the Si in the framework and maintaining electrical neutrality by stuffing the interstices in the framework with K, Na or both. Of course, the structure is not indifferent to the substitution of Al for Si and then K, Na-stuffing. The framework undergoes a displacive distortion. Also, the structures are subject to variation associated with Al–Si ordering on the tetrahedral sites and Na–K ordering in the interstices.

A c-axis projection of several unit cells of high tridymite is illustrated in Figure 2a. The silicate tetrahedra form (001) sheets in which each silicon shares three oxygens with neighboring silicons. The oxygens shared within a sheet lie in a plane. The fourth oxygen of each silicon (the apical oxygen) lies above or below the plane of the other three. The apical oxygens alternate above and below the sheet in adjacent tetrahedra. The apical oxygens are shared with other sheets stacked in the c direction. The maximum symmetry for this structure is $P6_3/m2/m2/c$ which is the space group for high tridymite. The mirrors perpendicular to c pass through the apical oxygens.

In the stuffed derivatives in the system $(Na,K)AlSiO_4$, the K and Na occupy the channels (parallel to the c-axis) outlined in Figure 2a by six-membered rings of tetrahedra. If the Al and Si are completely disordered on the tetrahedral sites, the maximum symmetry is $P6_3/m2/m2/c$.

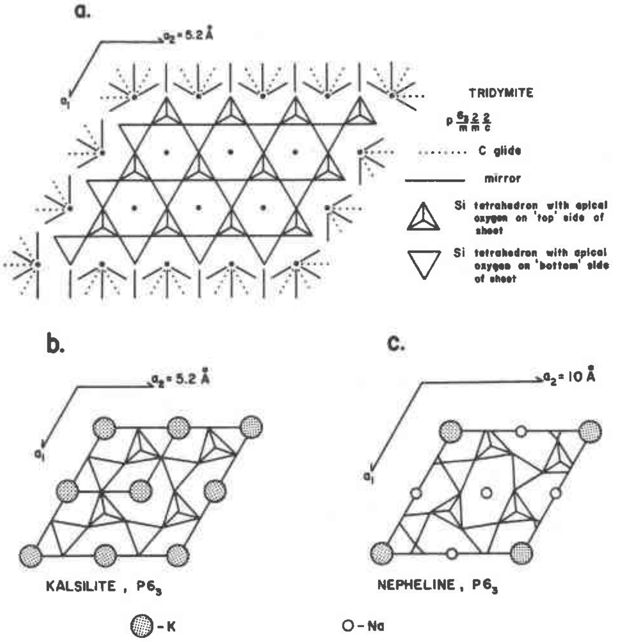

Fig. 2. The structures of tridymite and the stuffed derivatives, kalsilite and nepheline. In each case, a single (001) layer of tetrahedra is illustrated. a. 12 unit cells of tridymite. b. 4 unit cells of kalsilite showing the trigonal distortion of the interstices. c. 1 unit cell of nepheline. The interstices occupied by Na have 2-fold symmetry.

In the structural refinements of kalsilite (Perotta and Smith, 1965) and nepheline (Dollase, 1970; Foreman and Peacor, 1970; Hahn and Buerger, 1955) Al and Si are ordered according to the aluminum avoidance principle (Loewenstein, 1954). The Si tetrahedra are surrounded by Al tetrahedra and vice versa. It follows that, in a single (001) sheets, the Si tetrahedra are on one side of the sheet and the Al tetrahedra are on the other side. In the Al–Si ordered framework the (001) mirrors are not possible because they relate adjacent tetrahedra. For the same reason, 2-fold axes cannot exist parallel to **a** or [210]. The maximum possible symmetry is the acentric space group $P6_3mc$. This space group has not been reported in the $(Na,K)AlSiO_4$ system.

The structural refinements of kalsilite (Perotta and Smith, 1965) and nepheline (Dollase, 1970; Foreman and Peacor, 1970; Hahn and Buerger, 1955) show that the framework collapses around Na and K. In kalsilite, the shapes of the interstices in a single sheet projected down the **c**-axis are trigonal (Fig. 2b). In nepheline, the projected shapes of the interstices occupied by the smaller Na have 2-fold symmetry (Fig. 2c). In kalsilite, this distortion of the framework precludes mirror planes or glide planes parallel to **c**. The symmetry is $P6_322$ if Al and Si are disordered, or $P6_3$ if Al and Si are ordered.

The structures of the other polymorphs, O1, O2, H3, H4, synthetic kaliophilite and natural kaliophilite, are based on the high tridymite structure, presumably modified by different Al–Si ordering schemes or special combinations of distortions. The details of the structures are unknown. It is noteworthy that the lattice parameters of all of the polymorphs are related in a simple way to the unit cell of kalsilite (Smith and Tuttle, 1957). In each case, the *a* and *b* cell dimensions are either simple multiples of $a(\text{kalsilite}) = 5.2\text{Å}$ or simple multiples of $a(\text{kalsilite}) \times \sqrt{3} = 9\text{Å}$. The space groups of the polymorphs are all subgroups of $P6_3/m2/m2/c$. Kunze (1954) reported the space group $P222$ for the O1 polymorph. This space group is not compatible with the tridymite framework. For O1, I have reported the space group as $P222_1$, which is a subgroup of $P6_3/m2/m2/c$. The space group $P222_1$ precludes Al–Si ordering in compliance with the aluminum avoidance principle. Presumably, the orthorhombic O1 phase is Al–Si disordered.

Sample description

Kaliophilite from the volcanic ejecta of Monta Somma in Italy was examined. The sample was provided by the Harvard Geological Museum (sample #89597). The kaliophilite was identified and characterized by X-ray diffraction and electron diffraction.

The kaliophilite occurs in two habits, (1) radiating acicular and (2) anhedral, fine-grained granular. The former seems to have nucleated on the latter. The bulk composition of the kaliophilite is reported in Table 2. The analyses show traces of CaO and FeO, up to 1 wt.% Na_2O and a slight atomic excess of Si over Al. The space group for the kaliophilite, $P6_322$ (Lukesh and Buerger, 1942; and this study), precludes Al–Si ordering in accordance with the aluminum avoidance principle.

Methods of investigation

The results reported here are based partly on Transmission Electron Microscope (TEM) observations performed in 1983 in the Department of Biology at Appalachian State University. Some high temperature, single crystal X-ray experiments were performed in 1974 and 1975 at Harvard University.

The high temperature single crystal X-ray experiments were done using a precession camera equipped with a heater designed

Table 2. Electron microprobe analyses for kaliophilite

Wt. % oxides		Atoms / 4 oxygens	
SiO_2	38.87	Si	1.015
TiO_2	0.00	Al	0.981
Al_2O_3	31.89		
FeO	0.07	K	0.956
MnO	0.00	Na	0.039
CaO	0.05	Ca	0.002
K_2O	28.76	Fe	0.001
Na_2O	0.77		
SUM	100.41		

The analyses were performed by Timothy L. Grove at Harvard University and constructed by Timothy L. Grove. The single crystal was placed in a silica glass capillary which was then evacuated and sealed in order to minimize contamination and loss of K_2O and Na_2O. The capillary was then mounted in a goniometer head and the crystal was oriented in the conventional way. A stream of heated nitrogen gas was directed at the capillary from the heater mounted on the precession camera. The acicular kaliophilite was the only polymorph examined by this method. The temperature was measured by a thermocouple, calibrated against the melting points of grains of various pure crystalline substances mounted in the same way as the kaliophilite. At the highest attainable temperatures, on the order of 1100°C, the silica glass capillary would crystallize and fracture. Shortly after this, the single crystal would decrepitate due in part to the loss of K_2O. Limited, but useful information was obtained up to about 900°C.

The TEM experiments were performed on a Philips EM200 electron microscope. All observations were made with an electron acceleration voltage of 100 kV. The mineral samples were ground finer than 1 micron and were suspended in ethanol. The mineral grains were then deposited on the carbon support membrane of a copper grid by evaporating the ethanol from grids dipped in the suspension.

The electron microscope did not have a goniometer stage. This was somewhat of a disadvantage because the kaliophilite grains were randomly oriented. Correctly oriented grains were sought–tour de force–from the thousands of grains on each grid. Complicating matters even more, because the grains of kaliophilite have poor cleavage and are generally equant, they tend to change orientation when exposed to the electron beam. Near-centered Laue patterns were the best that could be obtained. The stereotilt was of little use in orienting crystals. Near-centered Laue patterns were measured using the method described by Gard (1976). In this way, the lattice constants were determined accurately and reliably for the kaliophilite. The "camera constant" for the electron microscope ($L\lambda$ = 12.73Åmm) was measured using nepheline, phlogopite and paragonite previously characterized by X-ray means. The measured lattice constants for the kaliophilite agree with values measured by X-ray diffraction of powdered samples and with values reported in the literature (Table 1).

Results

Because of the crystal orientation problem alluded to in the previous section, the TEM observations on kaliophilite are limited. Regardless of the orientation, in either bright field or dark field thin edges of the grains appear homogeneous up to 100000× magnification. The kaliophilite appears to be free of domain structures, twinning or other defects.

The high temperature X-ray experiments on kaliophilite revealed a simple, primitive lattice (Table 1) which persisted up to at least 850°C. This suggests that kaliophilite is not related to the other polymorphs by any simple displacive transformation. Above 850°C the material became amorphous due in part to the loss of K_2O.

The near **c**-axis and near **a**-axis electron diffraction patterns for the kaliophilite indicate a simple, primitive lattice (Fig. 3). The diffractions are for the most part sharp and easily resolved. There is no indication (Gard, 1976) that the very small reciprocal unit cell is an artifact of multiple diffraction or twinning.

Table 3 summarizes the diffraction characteristics of kaliophilite compared with the diffraction characteristics of kalsilite and synthetic kaliophilite. Each of these polymorphs possesses a 6_3 screw axis, which is indicated by the absence of the odd *l* (00*l*) diffractions. Kalsilite has no additional absences. For the synthetic kaliophilite, which has the same unit cell volume as kalsilite, a *c*-glide perpendicular to [210] is indicated by the systematic absence of the odd *l* (*hhl*) diffractions. The space group for the synthetic kaliophilite is $P6_3mc$ if Al and Si are ordered or $P6_3/m2/m2/c$ if Al and Si are disordered. The high temperature of formation for the synthetic kaliophi-

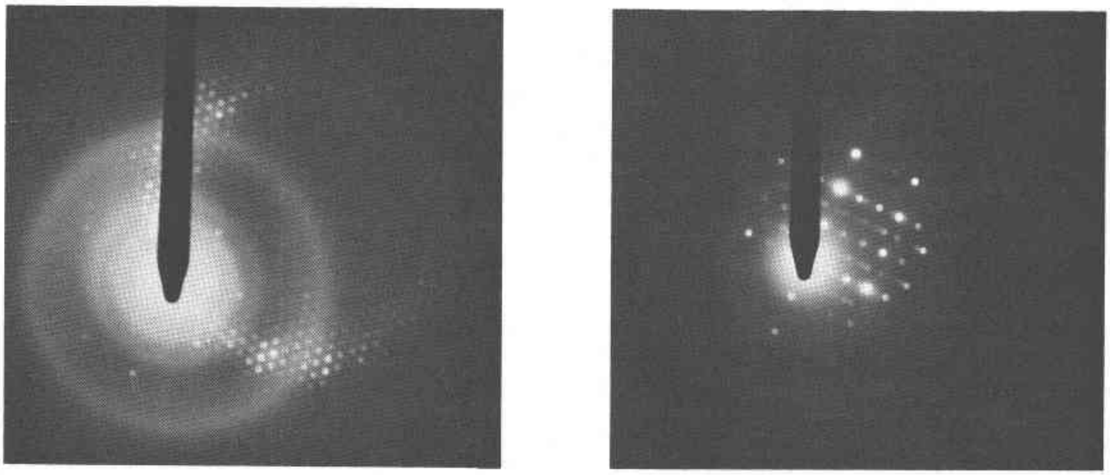

Fig. 3. Electron diffraction patterns. a. Near **c**-axis for kaliophilite. b. Near **a**-axis for kaliophilite.

Table 3. Summary of diffraction characteristics of kaliophilite, kalsilite and synthetic kaliophilite

	Unit cell geometry	Systematic extinctions (and weak diffractions)	Most likely space groups
Kaliophilite	primitive hexagonal a = 26.9 A, c = 8.5 A	(00l), l=2n+1 = 6_3 (h0l), l=2n+1, h=9n = Very weak or absent, indicating substructure like synthetic kaliophilite, with c-glide. All other odd l (h0l) diffractions are weak.	P 6_3 2 2 (Lukesh and Buerger, 1947) near P 6_3/m 2/c 2/m
*Synthetic kaliophilite	primitive hexagonal a = 5.2 A, c = 8.6 A	(00l), l=2n+1 = 6_3 (hhl), l=2n+1 = c-glide perpendicular to [210].	P 6_3/m 2/m 2/c or P 6_3 m c
Kalsilite	primitive hexagonal a = 5.2 A, c = 8.7 A	(00l), l=2n+1 = 6_3 no further extinctions.	P 6_3

* Diffraction characteristics for synthetic kaliophilite are from Smith and Tuttle (1957).

lite (Tuttle and Smith, 1958) suggests that the synthetic kaliophilite may be Al–Si disordered; hence, the space group would be $P6_3/m2/m2/c$, but the space group $P6_3mc$ certainly cannot be ruled out.

In the near a-axis electron diffraction pattern for kaliophilite (Fig. 3b), all odd l ($h0l$) diffractions are weak. This suggests a pseudo-or near c-glide perpendicular to **a**. Except where h = 9n, these diffractions are clearly visible, however weak. Although the space group is reported as $P6_322$, the structure must be close to $P6_3/m2/c2/m$. The odd l ($h0l$) diffractions where h = 9n are extremely weak or absent. The d-values for these extremely weak or absent diffractions of kaliophilite are the same as the d-values for the absent diffractions of synthetic kaliophilite (Smith and Tuttle, 1957). This indicates that the substructure of kaliophilite possesses the c-glide of the synthetic kaliophilite. Presumably, the kaliophilite transformed from some high temperature Al–Si disordered polymorph, very possibly the Al–Si disordered $P6_3/m2/m2/c$ polymorph.

Interpretation

Figure 4 shows the relationships between possible hexagonal space groups for the KAlSiO$_4$ stuffed derivatives of tridymite. Each space group places different constraints on Al–Si ordering and the type of distortion of the framework. Space groups $P6_3/m2/m2/c$ and $P6_322$ preclude Al–Si ordering. Polymorphs with the space groups $P6_3mc$ and $P6_3$ may be Al–Si ordered. The space groups $P6_3/m2/m2/c$ and $P6_3mc$ preclude distortion of the framework. Polymorphs with the space groups $P6_322$ and $P6_3$ may have distorted frameworks. One polymorph may be converted to another as the result of either changes in Al–Si order or displacive transformation. These two phenomena are not necessarily dependent. Only certain pairs of space groups are related by simple transformations involving only Al–Si order–disorder or only displacive distortion. The simple transformations are $P6_3/m2/m2/c$ – $P6_3mc$, $P6_3mc$ – $P6_3$, $P6_3/m2/m2/c$ – $P6_322$ and $P6_322$ – $P6_3$. The remaining transformations, $P6_3/m2/m2/c$ – $P6_3$ and $P6_3mc$ – $P6_322$, are less likely because they involve simultaneous Al–Si ordering and displacive distortion of the framework.

The structure of kalsilite and the diffraction patterns for kalsilite, kaliophilite and synthetic kaliophilite suggest the transformations $P6_3/m2/m2/c$ – $P6_3mc$ and $P6_3mc$ – $P6_3$. The relationships between the space groups and Al–Si ordering are illustrated qualitatively in Figure 5. For the basic hexagonal unit cell having the volume of the kalsilite unit cell (c = 8.6Å, a = 5.3Å), there are two tetrahedral sites for $P6_3$, each of multiplicity 2, and two for $P6_3mc$, each of multiplicity 2, but only one site of multiplicity 4 for $P6_3/m2/m2/c$. In Figure 5, the two sites in $P6_3$ (kalsilite) and $P6_3mc$ are designated T1 and T2. It is proposed that the tetrahedral site (T) in the Al–Si disordered $P6_3/m2/m2/c$ polymorph splits into two sites, T1 and T2, during cooling as the result of Al–Si ordering. With further cooling and ordering the occupancies of the two sites become more distinct. The displacive transfor-

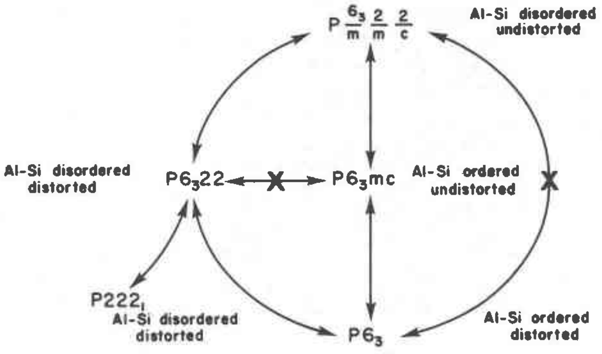

Fig. 4. The relationships between the possible space groups for the KAlSiO$_4$ stuffed derivatives of tridymite. Polymorphic transformations are indicated by double arrows. Unlikely transformations are marked with X's.

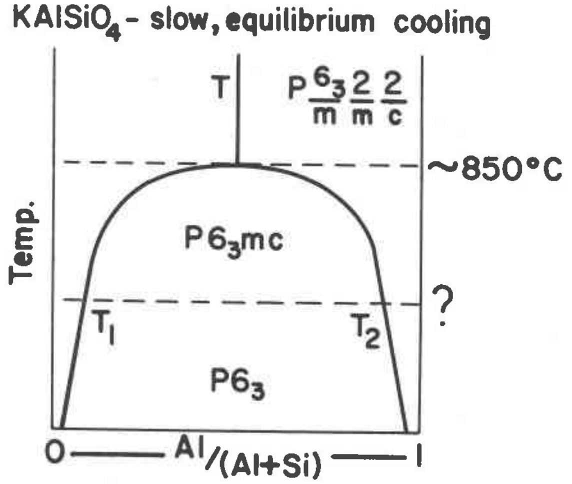

Fig. 5. Temperature-ordering diagram for $KAlSiO_4$. At high temperature, there is one tetrahedral site (T) and the space group is $P6_3/m2/m2/c$. Below 850°C, this site splits into two sites, T1 and T2. The T1 site is favored by Si, the T2 site is favored by Al, and the symmetry is reduced to $P6_3mc$.

mation, $P6_3mc - P6_3$, takes place at a temperature below the onset of ordering. Figure 6 is a reinterpretation of the phase relationships on the binary $KAlSiO_4$–$NaAlSiO_4$ consistent with the findings of this investigation.

The space group $P6_322$ for kaliophilite precludes long range Al–Si ordering that obeys the aluminum avoidance principle, suggesting that kaliophilite formed from the high temperature $P6_3/m2/m2/c$ polymorph. The kaliophilite may have short range Al–Si order in unit cell scale modulated domains of the $P6_3mc$ polymorph, domains related by twinning. If so, such twin domains were overlooked in the TEM examination perhaps because the anticipated size of the domains is so small or perhaps because of poor contrast between domains. The possibilities for twinning are discussed in the next section. In any case, the kaliophilite is probably a transitional state between $P6_3/m2/m2/c$ and $P6_3mc$. The synthetic kaliophilite may be either the hypothetical high temperature $P6_3/m2/m2/c$ polymorph or the intermediate temperature $P6_3mc$ polymorph.

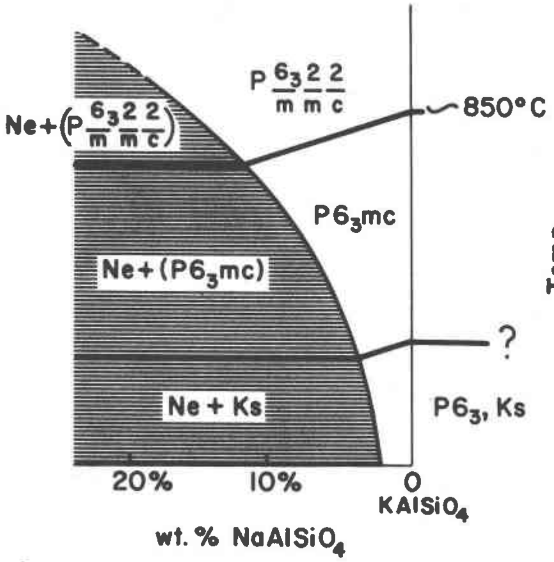

Fig. 6. Reinterpretated temperature–composition diagram for the potassic side of the $NaAlSiO_4$–$KAlSiO_4$ system.

The high temperature experiments showed that the kaliophilite unit cell persists up to approximately 850°C. Above this temperature, the kaliophilite became amorphous due in part to the loss of K_2O. The K_2O may have been lost in conjunction with the reorganization of the kaliophilite at the onset of a reconstructive transformation (Al–Si disordering?). If the kaliophilite represents a transitional state between $P6_3/m2/m2/c$ and $P6_3mc$, then the order-disorder transformation must take place at about 850°C.

Figure 7 is a hypothetical TTT (Time, Temperature, Transformation) diagram (Putnis and McConnell, 1980) for the $KAlSiO_4$ polymorphs. The Al–Si ordered poly-

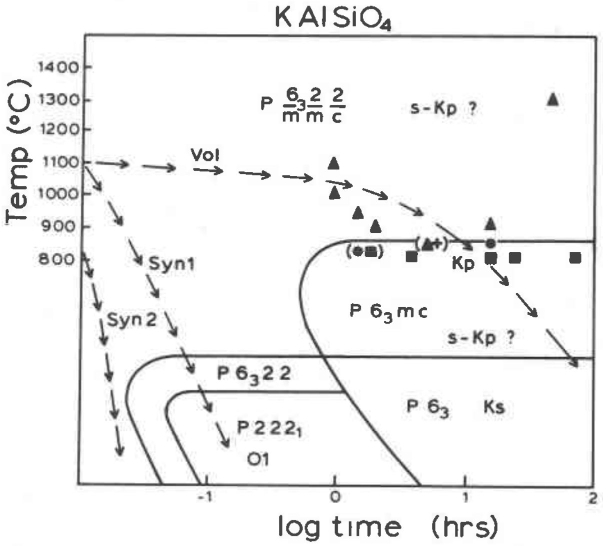

Fig. 7. Hypothetical TTT (Time–Temperature–Transformation) diagram for the $KAlSiO_4$ stuffed derivatives of tridymite. The dashed curves are hypothetical cooling histories for volcanic kalsilite (path Vol), for the orthorhombic O1 phase (path Syn 1) and for synthetic kaliophilite (path Syn 2). The abbreviations for the polymorphs are explained in Table 1. The filled triangles, circles, squares and the cross represent experiments reported by Tuttle and Smith (1958). The orthorhombic polymorph, O1, was identified in the quenched products of the experiments represented by the filled triangles. Kalsilite was identified in the quenched products of the experiments represented by the filled squares. The filled circles identify experiments which produced synthetic kaliophilite. The cross identifies the only experiment in which kaliophilite *may* have been produced.

morphs, $P6_3mc$ and $P6_3$, are enclosed by a c-shaped curve, which marks the onset of Al–Si ordering during cooling or by annealing. The upper temperature limit for the Al–Si ordered polymorphs, approximately 850°C, is based in part on the experimental work of Tuttle and Smith (1958) where I have reinterpreted the high temperature Al–Si ordered polymorph as $P6_3mc$ and the high temperature Al–Si disordered ploymorph as $P6_3/m2/m2/c$. A displacive transformation divides the ordered region into two parts, $P6_3mc$ and $P6_3$, and also divides the disordered region into two parts, $P6_3/m2/m2/c$ and $P6_322$. The equilibrium polymorphs are $P6_3/m2/m2/c$, $P6_3mc$ and $P6_3$. The other polymorphs in the diagram are unstable relative to these and given sufficient annealing time will transform to the more stable states. The orthorhombic phase, O1, is interpreted as a low temperature metastable polymorph. Hypothetical cooling histories are shown for volcanic kalsilite (path Vol) and for the synthetic polymorphs, O1 (path Syn 1) and synthetic kaliophilite (path Syn 2). I suggest the natural kaliophilite represents the transitional state marked Kp on the volcanic path.

Twinning in kalsilite?

Rotation twins and mirror twins should occur in kalsilite which has transformed from the hypothetical high temperature $P6_3/m2/m2/c$ polymorph. Unfortunately, I did not have access to kalsilite, of bona fide high temperature origin, suitable for the identification of the features by TEM. Such material may provide the best, direct verification of the relationships depicted in Figures 5, 6 and 7.

Rotation twins should occur in response to Al–Si ordering in domains, where the twin boundaries would be Al–Si disordered. This is best appreciated by considering the Al–Si ordering in a single (001) sheet of tetrahedra (Fig. 8). The ordered region on the left has the Al's on the "top" side of the sheet, and the Si's on the "bottom" side. Successive sheets of tetrahedra are stacked in the **c** direction, each with the Al's on the top and the Si's on the bottom. The domain on the right has the Si's on the top side and the Al's on the bottom side of each successive sheet of tetrahedra. The twin domains are related by a 2-fold axis parallel to a_1, a_2 or a_3 or by inversion (Fig. 8). Adjacent tetrahedra on either side of the twin boundary would have the same site occupancy, Al–O–Al or Si–O–Si. Except for the sodic nephelines which often have substantial excess SiO_2 (Hamilton and McKenzie, 1960), the other stuffed derivatives of tridymite lie approximately on the join $NaAlSiO_4$–$KAlSiO_4$. This suggests that, if present, the rotation twin boundaries are conservative on the average. Excess SiO_2 may be accommodated favorably along the twin boundaries because the Si–O–Si

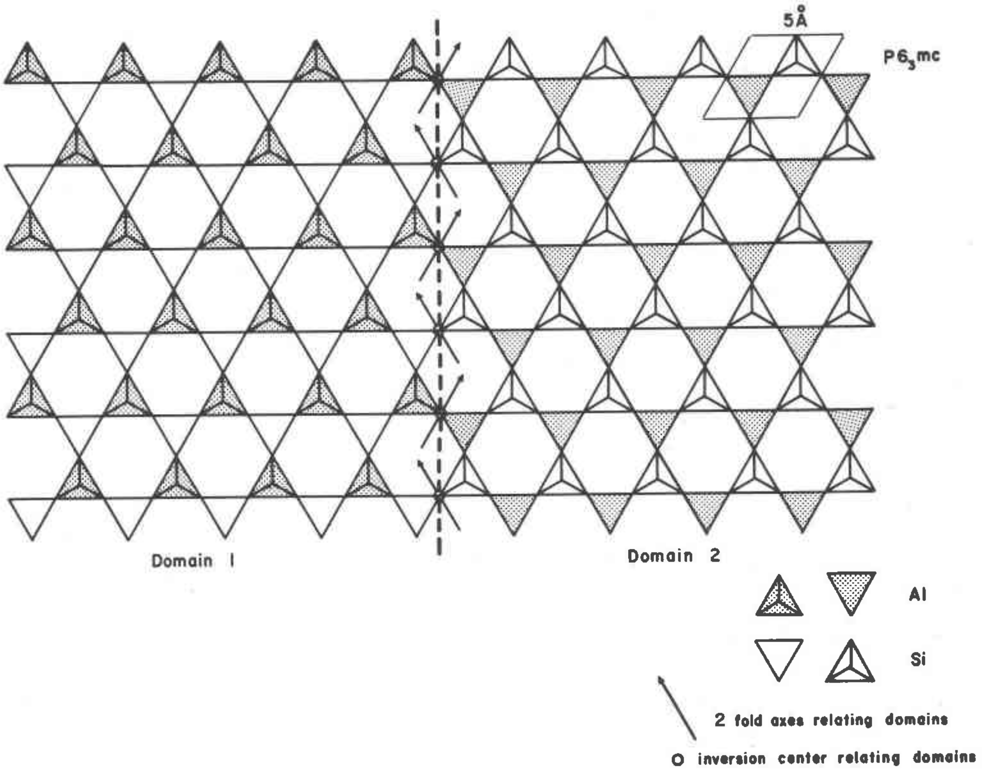

Fig. 8. Rotation twins in kalsilite. The hypothetical Al–Si ordered $P6_3mc$ structure projected onto the (001) plane, showing two domains. The twin domains are related by inversion or by 2-fold axes perpendicular to **c**.

configuration is stable, and may be thought of as tridymite which is restricted to the boundary surface.

Mirror twins in kalsilite would be a natural consequence of the displacive collapse of the framework associated with the $P6_3mc$ – $P6_3$ transformation. In a single (001) sheet of tetrahedra (Fig. 9), there are two ways a hexagonal interstice can distort to the trigonal, collapsed shape. The displacive distortion would occur at different places in the sheet according to either option, leading to twin domains related by mirror planes, (110), $(\bar{1}20)$ and $(\bar{2}10)$.

Conclusions

The structure of kalsilite and diffraction patterns for kalsilite, kaliophilite and synthetic kaliophilite suggest two transformations relating three polymorphs, in order from high temperature to low, $P6_3/m2/m2/c$ – $P6_3mc$ – $P6_3$. The evidence presented here for these transformations is difficult to reconcile with the high temperature orthorhombic polymorph, O1, suggested by Tuttle and Smith (1958). It is suggested here that O1 is a metastable low temperature polymorph, produced by rapid quenching of the hypothetical, high temperature $P6_3/m2/m2/c$ polymorph. The suggested relationships are illustrated in the schematic TTT diagram of Figure 7. This reevaluation of the phase relationships conforms with the fundamental crystal-chemical principle that the high temperature polymorph has a higher density of symmetry elements than the low temperature polymorph. In the case of the $KAlSiO_4$ polymorphs, addition of symmetry elements to kalsilite ($P6_3$) necessarily involves Al–Si disordering, displacive "undistortion" of the framework, or both.

The kaliophilite represents a transitional state between $P6_3/m2/m2/c$ and $P6_3mc$. The very large unit cell may be due to very fine scale modulated domains of the hypothetical $P6_3mc$ polymorph.

By inference, the binary polymorphs H3, H4 and O2 are metastable low temperature polymorphs. The stable binary high temperature polymorph is most likely nepheline or the hypothetical $P6_3/m2/m2/c$ polymorph with approximately the same unit cell volume as kalsilite. The stable high temperature $KAlSiO_3$ polymorph may be represented by the so-called synthetic kaliophilite. The possible, revised relationships for the binary system are shown in Figure 6.

The determination, at high temperature, of the space groups and lattice constants of the various polymorphs would be particularly useful in testing these hypothetical relationships.

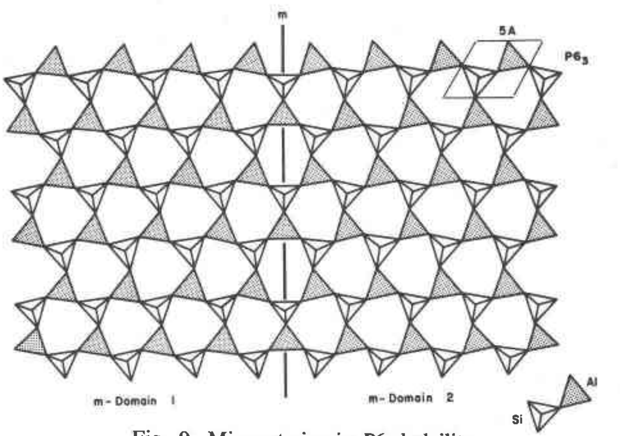

Fig. 9. Mirror twins in $P6_3$ kalsilite.

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