

Phase transitions and microstructures in natural kaliophilite

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Abstract : An investigation using TEM, high temperature X-ray powder diffraction and high temperature single-crystal X-ray diffraction revealed previously unreported microstructures and phase transitions in natural kaliophilite. Measurements of unit cell dimensions from room temperature to 895°C indicate the existence of a displacive phase transition at ~ 725°C between two hexagonal phases with the same unit cell. A symmetry change of $P6_322 \rightleftharpoons P6_3$ is tentatively suggested with the concomitant development of merohedral twins. Spontaneous strain determinations suggest that the transition is close to being tricritical in character. Above ~ 750°C kaliophilite crystals undergo a first order epitaxial phase transition to a different hexagonal phase with $a = 8.9 \text{ \AA}$ and $c = 8.4 \text{ \AA}$. Dark and bright field images in the TEM show the presence of twins and heterogeneously distributed linear defects. These are interpreted respectively as transformation twins and stacking defects incorporated during crystal growth. The thermal evolution of kaliophilite is sufficiently different from that of kalsilite to indicate that it has a different framework topology and is not a true stuffed tridymite structure.

Key-words : kaliophilite, phase transitions, spontaneous strain, transmission electron microscopy, microstructures.

1. Introduction

The compound KAlSiO_4 appears to occur in several modifications, (Table 1) two of which, kalsilite and kaliophilite, occur in nature. Kalsilite is found almost exclusively in K-rich silica undersaturated volcanic rocks, while kaliophilite is known only from ejected blocks incorporated into pyroclastics. The type locality of kaliophilite is in biotite pyroxenite ejecta from Mt. Vesuvius (Bannister, 1931), but it has also been observed in ejecta belonging to different pyroclastic formations in the Alban Hills (Barbieri *et al.*, 1970), where it is associated mainly with such minerals as clinopyroxene, garnet, melilite, leucite, haüyne and latiumite. In the equilibrium phase diagram

for NaAlSiO_4 - KAlSiO_4 proposed by Tuttle & Smith (1958), natural kaliophilite with a large unit cell ($a = 27.01$, $c = 8.56 \text{ \AA}$) is treated as a metastable phase at atmospheric pressure at all temperatures. Its relationships to the other phases are not clearly understood, however, and the occurrence of kaliophilite in ejected blocks does not preclude its having a true stability field at higher pressures. It may also be stabilised relative to kalsilite by solid solution toward nepheline.

The known phases of KAlSiO_4 are all tectosilicates and are characterized by stacking of layers of six-membered rings of $[\text{AlO}_4]$ and $[\text{SiO}_4]$ tetrahedra, with K^+ in the framework cavities as the charge-balancing cation. These structural features produce unit-cell parameters which are related in

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Table 1. Natural and synthetic phases of KAlSiO_4 .

Phase	most likely symmetry	a(Å)	b(Å)	c(Å)	ref
kalsilite (high)	$P6_3mc$	5.30		8.65	a
kalsilite	$P6_3$	5.16		8.69	b
kalsilite (supercell)	$P6_3$	8.94		8.69	c
$3\sqrt{3}$ kalsilite	orthorhombic	27.42	5.28	8.66	d
orthorhombic O1	$Pn2_1m$	15.67	9.07	8.56	e
orthorhombic O1 (high)	$Pbm2, Pb2m, Pbcm$	15.60	18.11	8.56	f
KAlSiO_4 - $Icmm$	pseudo-orthorhombic	10.55	18.15	8.49	g
synthetic kaliophilite	$P6_3mc$ or $P6_322$	5.18		8.56	h, i
natural kaliophilite	$P6_322$ or $P6_3/m$	27.01		8.56	l, m

Because there is no generally accepted nomenclature for KAlSiO_4 polymorph we have chosen to follow the nomenclature used by Capobianco & Carpenter (1989). a - Andou & Kawahara (1982). b - Perrotta & Smith (1965). c - Smith & Sahama (1957). d - Capobianco & Carpenter (1989). e - Gregorkiewitz & Schafer (1980). f - Cook *et al.* (1977). g - Minor *et al.* (1978). h - Abbott (1984). i - Smith & Tuttle (1957). l - Lukesh & Burger (1947). m - Alberti & Gregorkiewitz, reported in Merlino (1984).

a simple geometric way for all the phases. The a and b parameters are metrically related to the distance between centers of the six-membered rings of tetrahedra. This distance is approximately 5.2 Å and is the a dimension of the kalsilite unit cell. Values of a and b for the other polymorphs are then multiples of A or of $A\sqrt{3}$. (Throughout this paper we use A and C to refer to the a and c parameters of the basic kalsilite structure). Along the crystallographic c -axis, the rings are stacked as in tridymite with a c -repeat of ~ 8.6 Å, which corresponds to two layers of tetrahedra joined by shared apical oxygens.

So far KAlSiO_4 polymorphs are known to have at least three topologically different modifications (Fig. 1). Kalsilite (Perrotta & Smith, 1965) itself has the framework topology of high tridymite: all the rings have tetrahedra pointing alternately up and down. This is denoted as UDUDUD, where U and D represent tetrahedra pointing up and down respectively. O1- KAlSiO_4 , (Gregorkiewitz & Schäfer, 1980) which is orthorhombic, is the stable polymorph at high temperatures and its structure is based on two different ring topologies, UUDDUD and UUDDDD, in the proportion 2:1. Finally, the phase known as KAlSiO_4 - $Icmm$ (Minor *et al.*, 1978), prepared by cation exchange from orthorhombic RbAlSiO_4 , has a framework of UUDDDD rings. Which, if any, of these topologies is correct for kaliophilite is not yet known, though the unit cell dimensions are most closely related to those of kalsilite. Nor-

mal kaliophilite has a hexagonal cell with $c \approx C$, $a \approx 3A\sqrt{3}$; the a repeat is a threefold repeat along a direction 30° from the a -axis of kalsilite. The space group as been determined as $P6_322$ from single crystal X-ray diffraction data by Lukesh & Burger (1942), but according to the electron diffraction study of Abbott (1984) the structure may be close to $P6_3/mcm$. Other variants are known, however. Tilley & Henry (1953) have reported a kaliophilite from the Alban Hills for which reflections of the type $k = 3n$ were diffuse (Smith & Tuttle, 1957). But Bonaccorsi (1988), who has recorded a^*b^* electron diffraction patterns on kaliophilite of the Alban Hills, often observed diffuseness only for the reflections of the type $h-k = 3n \pm 1$. Kaliophilite was also synthesized by Smith & Tuttle (1957) during their investigation of the nepheline-kalsilite system, but their synthetic sample was not identical to natural kaliophilite. The intensity distribution of the powder pattern matched that of kaliophilite but the cell parameters were $a \approx A$, $c \approx C$. So far unit cell parameters of synthetic kaliophilite are based only on powder diffraction data which is not a conclusive test, however.

Phases with open framework structures such as tridymite, nepheline and kalsilite characteristically show a variety of phase transitions in response to changing temperature and pressure. Kalsilite itself shows two apparently reversible transitions, at 850 and 920°C, (Capobianco & Carpenter, 1989) before transforming irreversibly

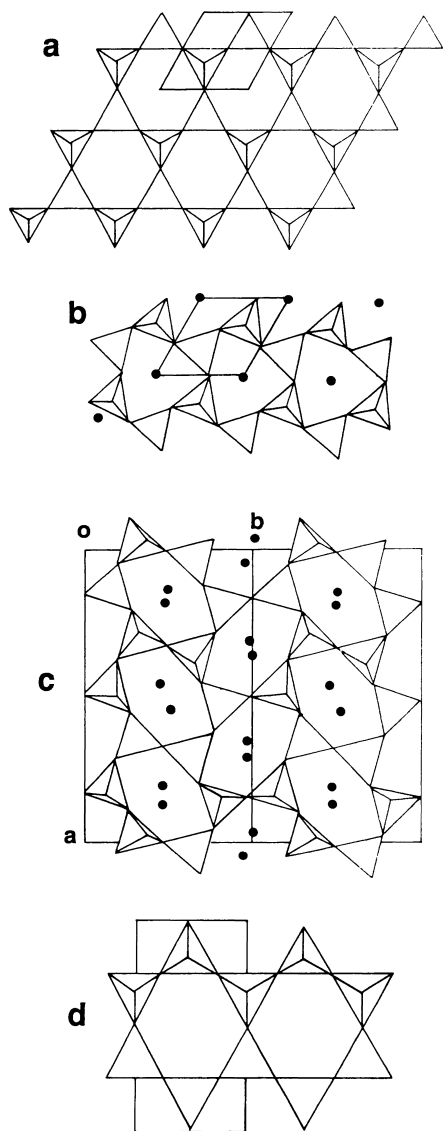


Fig. 1 a-d. Schematic drawings of the framework topologies viewed down the crystallographic *c*-axis; a - high tridymite, b - kalsilite, c - OI-KAlSiO₄, d - undistorted layer found in KAlSiO₄ phase of the *Icmm*-type. Filled circles are K. In Fig. 1d the K atoms have been left out.

to OI-KAlSiO₄ above ~ 950°C (Tuttle & Smith, 1958). There is some doubt about the space groups of these structures because of the presence of twinning on an electron optical scale, but the symmetry of "high" kalsilite at 950°C is con-

sistent with *P6₃mc* (Kawahara *et al.*, 1987). OI-KAlSiO₄ also shows evidence of reversible and presumably displacive transitions at ~ 420 and ~ 540°C (Lange *et al.*, 1986; Capobianco & Carpenter, 1989). If NaAlSiO₄ component is added in solid solution the structures observed at room temperature change and it seems likely that different sequences of phase transitions as a function of temperature will also occur. Natural kaliophilites have compositions in the range ~ Ne₁₉Ks₈₁ to ~ Ne₀Ks₁₀₀ (Barbieri *et al.*, 1970), where Ne and Ks refer to the NaAlSiO₄ and KAlSiO₄ components respectively.

From this brief summary, it is evident that many unanswered questions remain concerning the structures and stability relations of phases with compositions close to KAlSiO₄. The aims of the present study were (a) to characterise natural kaliophilite by transmission electron microscopy and (b) to examine its structural variations as a function of temperature. Observations of microstructures which are interpreted as growth defects and transformation twins, and the identification of a discrete phase transition at ~ 725°C, demonstrate that kaliophilite behaves quite differently from kalsilite both in nature and in laboratory experiments.

2. Sample description

The kaliophilite examined in this study was separated from a volcanic ejectum of Mt. Vesuvius containing augite and biotite (Harker collection, specimen n° 52732, Department of Earth Sciences, Cambridge). The kaliophilite occurs in two habits: acicular bundles, up to 4 mm long, in the cavities of the rock associated with crystals of black augite and dark brown biotite and as interlocking crystals elongated along *c* forming 20 to 30% of the matrix. In thin section large kaliophilite grains cut perpendicular to their *c*-axis are divided into smaller, slightly mis-oriented domains with no obvious crystallographic relationships between them. In sections parallel to the *c*-axis these subgrains are elongate and delimited by planar boundaries parallel to *c*. Compositions were determined by a Cameca SX50 probe using a wavelength-dispersive system for Na and a energy-dispersive system for Si, Al, Fe, Mg, Ca, K. The acceleration voltage was 20 kV and the beam current was 10 nA. Electron microprobe analyses from different grains gave an average composition of Na_{0.05}

Table 2. Chemical analysis of kaliophilite (average of 10 electron microprobe analyses).

	Number of ions	
	wt%	for 4 oxygens
SiO ₂	38.73	Si 1.02
Al ₂ O ₃	31.55	Al 0.98
FeO	0.21	Fe 0.01
MgO	0.00	Mg -
CaO	0.00	Ca -
Na ₂ O	1.04	Na 0.05
K ₂ O	28.07	K 0.94
SUM	99.60	
		Ks 94.67
		Ne 5.33

K_{0.95}AlSiO₄ (Table 2). No significant compositional variations within individual grains or between grains were detected. An infra-red spectrum was collected to check for the presence of water or structurally bound hydroxyl; no evidence was found for either.

3. Experimental methods

3.1. Powder X-ray methods

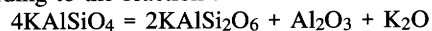
The X-ray measurements were made with a multichannel CPS-120 diffractometer, using CuK α_1 radiation and a quartz monochromator. The sample support, a strip of platinum, was used as a resistance heater. Temperature was monitored using a platinum -13% rhodium thermocouple welded to the underside of the strip, and calibrated against the transition points of various standards mounted in the same configuration. The uncertainty of the temperature scale was estimated as $\pm 10^\circ\text{C}$ but the temperature stability of the furnace was always within 1°C . Al₂O₃ was used as an internal standard for 2θ and all the heating runs were carried out in air. Each powder diffraction spectrum took 3-4 hours to collect and lattice parameters were determined by least-squares refinement using 23 peak positions. The cell parameters at room temperature were also refined from film data recorded with a Huber 621 Guinier powder camera as a check of the data from the multichannel diffractometer. The results of the lattice parameter refinements are given in Table 3.

Table 3. Unit cell data for kaliophilite.

T ($^\circ\text{C}$)	a ($\text{\AA}$)	c ($\text{\AA}$)	V ($\text{\AA}^3$)
25*	27.011 (2)	8.557 (1)	5406 (1)
25	27.027 (4)	8.563 (3)	5417 (2)
150	27.074 (4)	8.583 (3)	5449 (2)
200	27.093 (4)	8.595 (3)	5464 (2)
250	27.115 (4)	8.599 (3)	5475 (2)
300	27.140 (4)	8.610 (3)	5493 (2)
350	27.164 (4)	8.620 (2)	5508 (2)
400	27.185 (3)	8.626 (2)	5521 (1)
450	27.208 (4)	8.640 (2)	5539 (2)
500	27.236 (3)	8.645 (2)	5554 (1)
575	27.274 (3)	8.665 (2)	5582 (1)
600	27.290 (3)	8.671 (2)	5592 (1)
625	27.303 (2)	8.675 (2)	5601 (1)
650	27.320 (3)	8.683 (2)	5613 (1)
675	27.337 (3)	8.691 (2)	5624 (1)
700	27.351 (3)	8.701 (2)	5637 (1)
725	27.366 (3)	8.708 (2)	5648 (1)
750	27.378 (3)	8.712 (2)	5655 (1)
775	27.389 (3)	8.711 (2)	5659 (1)
790	27.393 (3)	8.713 (2)	5662 (1)
805	27.391 (3)	8.718 (2)	5665 (1)
820	27.400 (3)	8.717 (2)	5667 (1)
835	27.413 (3)	8.713 (2)	5670 (1)
850	27.422 (3)	8.714 (2)	5675 (1)
865	27.423 (2)	8.713 (2)	5675 (1)
880	27.431 (3)	8.717 (2)	5680 (1)
895	27.438 (4)	8.716 (3)	5683 (2)

* Refer to data from Guinier camera. Figures in brackets indicate the uncertainty ($\pm 1\sigma$) in the last digit.

Powder patterns collected at around 900°C contained very weak leucite diffraction lines. At still higher temperatures leucite formation became more important and at about 1100°C all the kaliophilite was transformed to leucite. The formation of leucite is irreversible and is probably due to volatilization of K from the crystals according to the reaction:



Because of this decomposition of kaliophilite at high temperatures, we report the variation of the unit-cell parameters up to only 895°C .

3.2. High-temperature single-crystal X-ray methods

Colourless transparent kaliophilite crystals oc-

curing as hexagonal prisms elongated along their *c*-axis were examined by the X-ray precession method at room temperature and at high temperatures. Each crystal was attached to the top of a silica glass capillary with a high temperature ceramic adhesive and then mounted on a "STOE" precession camera. A standard cylindrical furnace assembly with a horseshoe shaped heating element was positioned around the sample, with a thermocouple a few millimeters from the crystal. The furnace contained only small entrance and exit windows for the X-ray beam in order to ensure an even temperature distribution. Exposures times of 1-2 weeks were used.

In a first series of experiments, precession photographs were collected at 200°C intervals up to 750°C over a period of 16 weeks. The high temperature photographs showed clear signs of degradation of the original kaliophilite crystal. At 600°C a few new diffuse spots appeared in the photograph in the direction of $[110]^*$, and at 750°C a change of unit cell dimensions was observed. We interpret these changes in terms of the epitaxial growth of a new, but closely related, hexagonal phase with $a \approx A\sqrt{3}$ and $c \approx C$. The transformation is irreversible. A second series of exposures was collected in which large crystals were heated rapidly to 775°C without the intermediate steps. We observed the same epitaxial phase transformation with less evidence of degradation of the crystal. The reciprocal lattice was recorded for the zero-layer a^*-b^* and $c^*-[110]^*$ planes. This irreversible behaviour was not considered relevant to the microstructures and reversible phase transition observed in kaliophilite and is not analysed any further in this paper.

3.3. Transmission electron microscopy

Kaliophilite grains were gently ground under alcohol and deposited on thin carbon support films of a copper grid by evaporating the alcohol from grids dipped in the suspension. TEM samples were prepared also from petrographic thin sections. Copper grids were glued on selected areas of the thin sections, removed from the thin section and then ion beam thinned. Two microscopes were used for the observations : a JEOL JEM 100CX and an AEI EMG microscope, both operating at 100kV. Kaliophilite is highly sensitive to electron beam damage. After exposure to the electron beam for ~ 30 seconds the crystals developed a speckled texture and the diffraction

patterns became diffuse. By using a defocussed beam to reduce the rate of damage, it was possible to photograph microstructures and diffraction patterns before the degradation became a serious problem, however. Dark field images were obtained with a relatively small (20 μm) objective aperture, but, because of the small re-

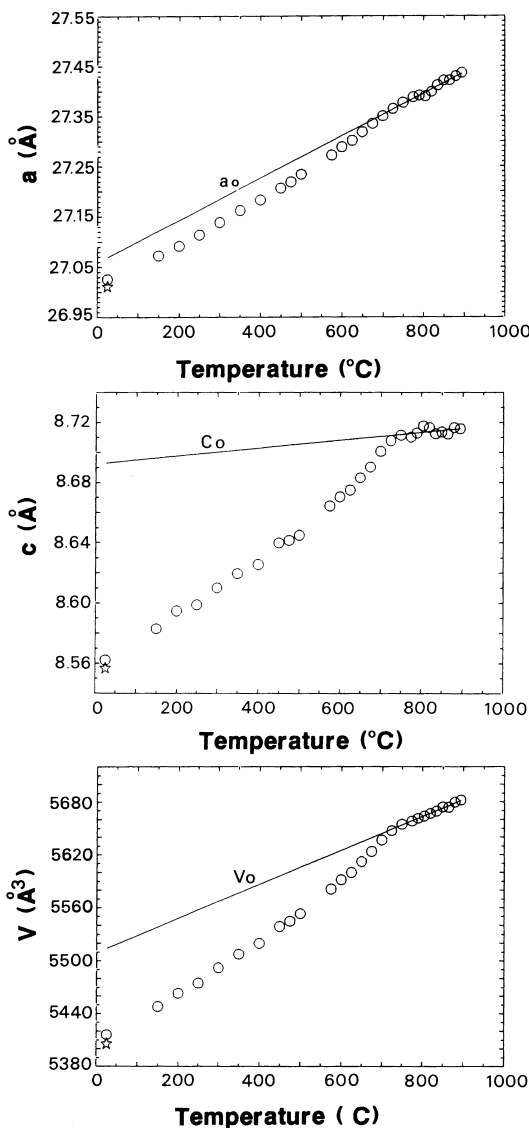


Fig. 2. Unit cell dimensions a , c and volume V as a function of temperature. Standard deviations ($\pm 1\sigma$) are within the size of the circles. Stars represent unit cell parameters from Guinier data; a_0 , c_0 and V_0 represent the unit cell parameters of the high-temperature phase extrapolated from high temperature.

ciprocal repeat, it was not usually possible to obtain images from a single superlattice reflection.

Heating experiments were carried out with an EM-SHH single tilt heating holder in the JEOL electron microscope. Foils of 3 mm diameter were heated by an annular molybdenum resistance furnace. Specimen temperatures could not be measured directly, but the furnace temperature was monitored through a platinum -13 % rhodium thermocouple spot welded to the furnace body. The furnace was heated up to 900°C at a rate of about 5°C per minute and allowed to stabilize for about 30 min before observations were begun. It is likely that temperature gradients of up to ~ 300°C per millimetre can exist in this type of furnace.

4. Results

4.1. X-ray diffraction

The temperature evolution of the refined unit cell parameters is illustrated in Fig. 2. A phase transition is seen to occur near 730°C and is characterized by a marked change in the thermal expansion. The change in lattice parameters was observed in both heating and cooling cycles suggesting that the transition is reversible. The

powder diffraction patterns showed no signs of peak broadening or splitting in the vicinity of the transition temperature. Nor was any evidence found for the appearance or disappearance of peaks due to kaliophilite. The transition thus appears not to involve a change in crystal system. This apparent lack of a change of diffraction symmetry was also consistent with the high temperature single crystal X-ray diffraction patterns.

The room temperature precession photographs confirmed the space group of $P6_322$ for our natural kaliophilite. The only systematic extinctions, $00l$ absent for $l = 2n + 1$, and the diffraction symmetry, $6/mmm$, lead to space group $P6_322$ as reported by Lukesh & Burger (1942). However, TEM observations regarding the ubiquitous presence of what we interpret as merohedral twinning (see below) must now be taken into account. The twinning may be responsible for the apparent $6/mmm$ diffraction symmetry and the real space group is probable of lower symmetry than $P6_322$. An obvious subgroup would be $P6_3$.

The irreversible transition to a different hexagonal phase was not observed in the powder diffraction experiments, probably because of the shorter time scale required to collect the powder data. From the single crystal observations, this new phase belongs to Laue group $6/mmm$ and the

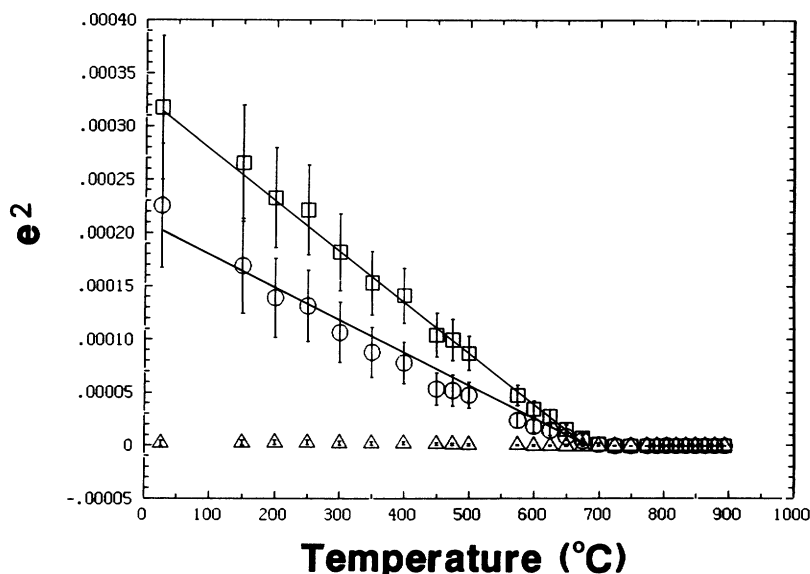


Fig. 3. Temperature evolution of the square of the spontaneous strains, e^2 , in kaliophilite. Triangle, open circle and square represent e^2_{11} , e^2_{33} and e^2_s respectively. Straight lines are least squares fits to the data given $T_c = 725 \pm 10^\circ\text{C}$.

cell dimensions are $a \approx A\sqrt{3}$ and $c \approx C$, that is 1/9 of kaliophilite unit cell.

With regard to the change in thermal expansion of kaliophilite at $\sim 725^\circ\text{C}$, we assume that the transition was between a hexagonal high symmetry phase and a hexagonal or trigonal low symmetry phase. No symmetry breaking strain therefore develops and the only spontaneous strain elements are non-symmetry breaking, with the relationships :

$$e_{11} = e_{22} \neq e_{33}$$

where e_{11} , e_{22} , e_{33} are defined as :

$$e_{11} = e_{22} = (a - a_0)/a_0$$

$$e_{33} = (c - c_0)/c_0$$

a_0 , c_0 are the parameters of high-temperature phase extrapolated from high temperatures down to the temperature at which a and c were measured. The volume strain is defined as :

$$V_s = (V - V_0)/V_0$$

where V is the unit cell volume of the low-temperature phase at a given temperature and V_0 is the unit cell volume of the high-temperature phase extrapolated to the same temperature from measurements made above the transition point. From Fig. 3 it is apparent that the square of all these strain parameters is linear with temperature, with an extrapolated transition temperature, T_c , of $725 \pm 10^\circ\text{C}$. The expected relationship be-

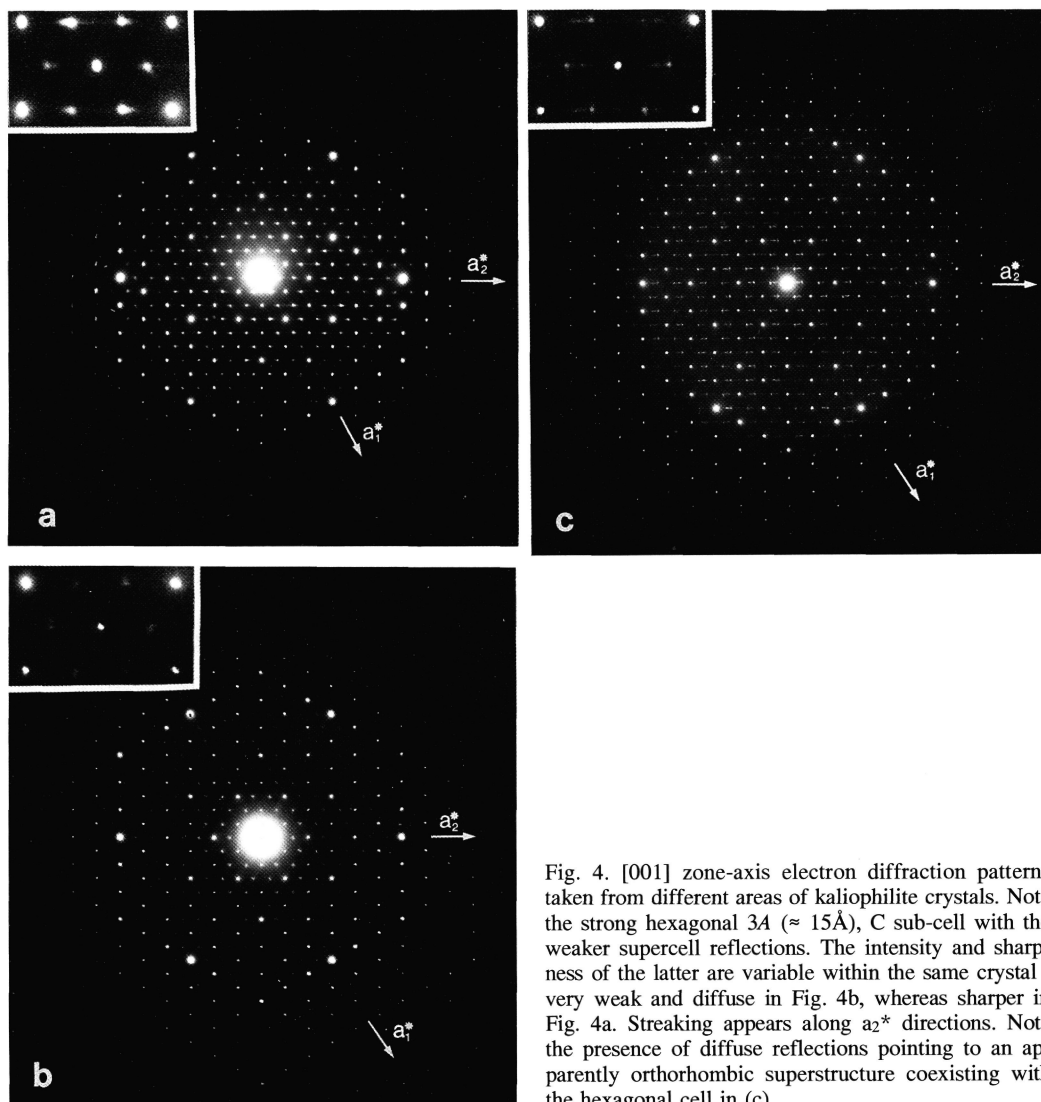


Fig. 4. [001] zone-axis electron diffraction patterns taken from different areas of kaliophilite crystals. Note the strong hexagonal $3A$ ($\approx 15\text{\AA}$), C sub-cell with the weaker supercell reflections. The intensity and sharpness of the latter are variable within the same crystal : very weak and diffuse in Fig. 4b, whereas sharper in Fig. 4a. Streaking appears along a_2^* directions. Note the presence of diffuse reflections pointing to an apparently orthorhombic superstructure coexisting with the hexagonal cell in (c).

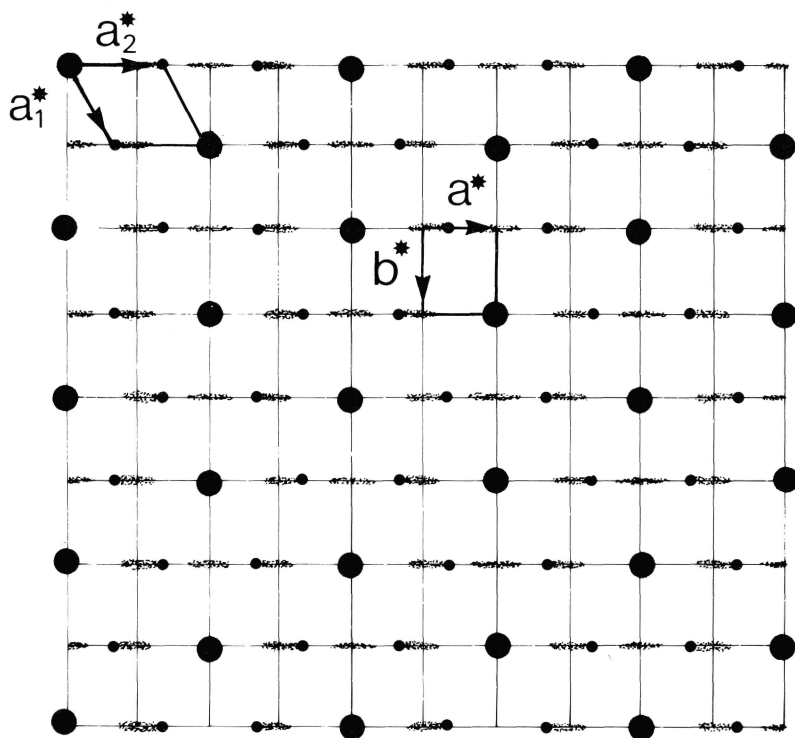


Fig. 5. Schematic diagram of Fig. 4c. The orthorhombic phase has $a^* = a_{\text{hex}}^* 3/4$ and $b^* = a_{\text{hex}}^* \sqrt{3}/2$ and is coexistent with hexagonal kaliophilite superstructure.

tween non-symmetry breaking strain and the order parameter, Q , for the transition is :

$$e_{11} \propto e_{22} \propto e_{33} \propto V_s \propto Q^2.$$

The transition thus appears to be close to tricritical in character [$Q^4 \propto (T_c - T)$]. In order to test this hypothesis the heat capacity of kaliophilite was measured by differential scanning calorimetry. The C_p data indicate a transition effect which is not of first order, but the scatter in the data at such high temperatures was large, and so we were unable to confirm the tricritical behaviour.

4.2. TEM observations

The $a^* \cdot b^*$ electron diffraction patterns of kaliophilite showed a strong hexagonal subcell ($3A$, C) with weak and often elongated $3A\sqrt{3}$, C supercell reflections (Fig. 4). In other words the reflections with $h \cdot k = 3n$ are strong and sharp, while the reflections with $h \cdot k \neq 3n$ are weaker and can exhibit streaking parallel to a^* . The subcell parameters ($3A$, C) are similar to the trikalsilite unit cell ($a = 15.4$, $c = 8.6$ Å) which represents a structural variant between nepheline and kalsilite

(Merlino, 1984 ; Bonaccorsi *et al.*, 1988). The intensity and sharpness of the supercell reflections were variable within the same crystal of kaliophilite (Fig. 4). In addition, the presence of a possible orthorhombic superstructure coexisting with hexagonal kaliophilite is suggested by the diffuse diffraction maxima shown in Fig. 4c. The orthorhombic phase has $a = a_{\text{kp}} 2/\sqrt{3} \approx 31.20$ Å and $b = a_{\text{kp}} \approx 27.02$ Å (Fig. 5). Two major zones containing c^* are shown in Fig. 6. Violation of the systematic absences due to the 6_3 axis are probably due to double diffraction in these patterns. Some streaking was observed in the planes perpendicular to c^* (Fig. 6b). On heating *in situ* up to a furnace temperature of 900°C for 1 day the superlattice reflections did not disappear.

Two general type of defects were observed in bright and dark field images. Domains with irregular shapes were seen only in orientations with the crystallographic c -axis close to being parallel to the electron beam (Fig. 7). Selected area diffraction from regions including the domains always gave a single crystal diffraction

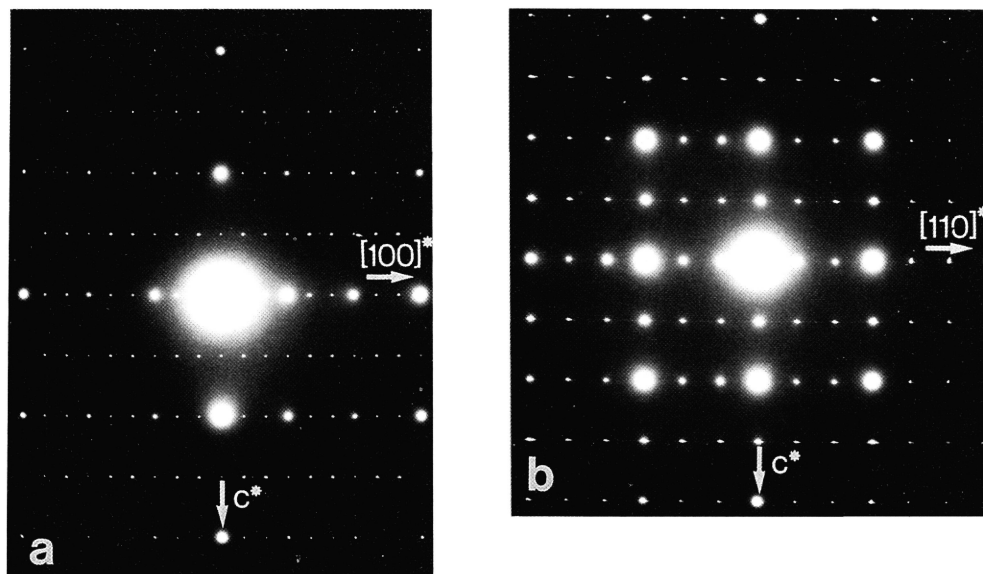


Fig. 6. Diffraction patterns of kaliophilite showing the $[100]^*c^*$ and the $[110]^*c^*$ reciprocal lattice plane in (a) and (b) respectively. Note the streaking perpendicular to c^* in (b).

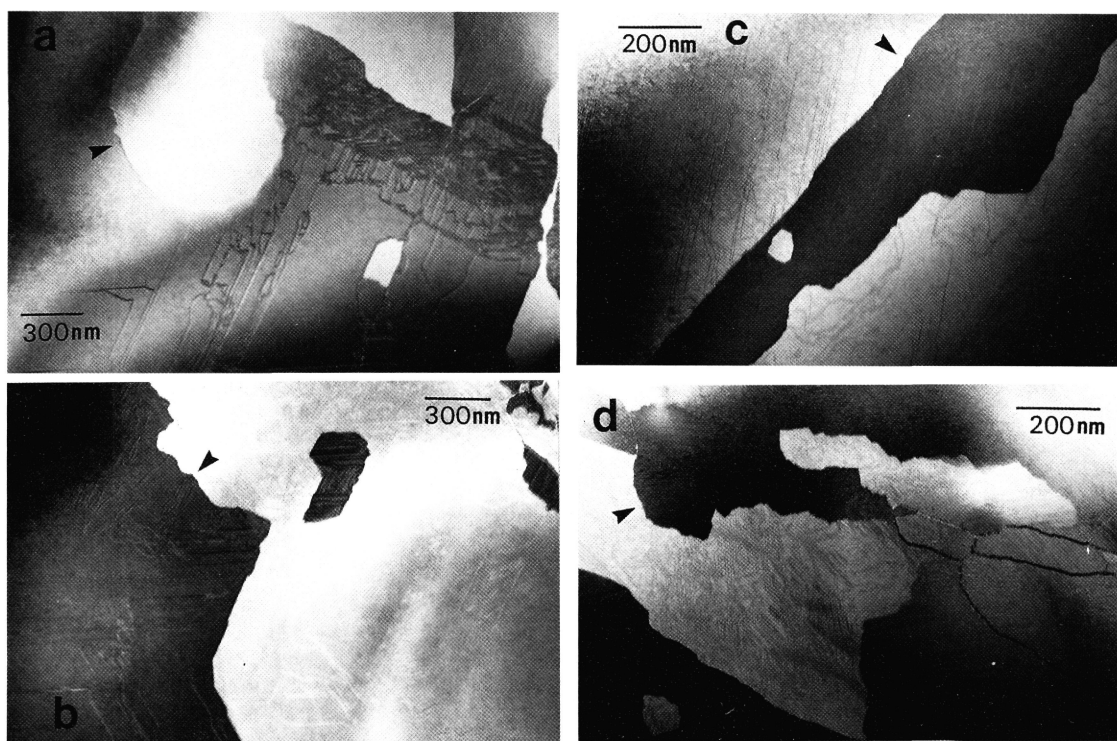


Fig. 7. Dark (a, b, c) and bright (d) field images near the $[001]$ zone-axis, showing large twin domains (black arrows) with numerous and heterogeneously distributed linear defects. Note that the linear defects are sometimes continuous across the twin boundaries.

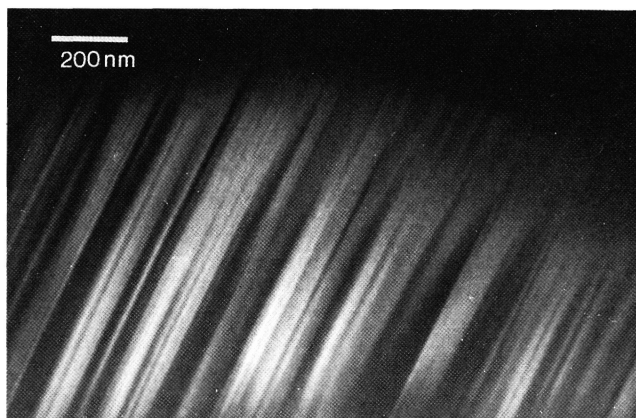


Fig. 8. Dark field image of linear defects which lie parallel to the c -axis in this orientation.

pattern without any splitting of spots. We interpret these domains as being merohedral twins. In order to determine whether they might be due to the reversible phase transition identified in the powder diffraction study, we examined sections showing the twin domains in the heating stage. The domains could still be seen at the maximum furnace temperature of 900°C . The actual temperature of the sample under these conditions was not known however.

Planar or irregularly shaped defects were observed in many bright and dark field images (Fig. 7, 8, 9). In sections close to having the c -axis parallel to the electron beam, these defects showed a highly heterogeneous distribution (Fig. 7). The defect density is variable within the same crystal of kaliophilite and this variability is probably responsible for the different degrees of diffuseness observed for superlattice reflections

in the electron diffraction patterns. In other sections, these defects appeared to be linear and parallel to the c -axis and are probably responsible for the streaking perpendicular to c^* in the electron diffraction patterns. The contrast conditions for these could not be fully characterized because of the rapid beam damage and because dark field experiments were limited by the small reciprocal lattice repeat. It was difficult to obtain dark field images from single reflections, but black and white contrast appeared to arise in dark field images obtained with reflections such as 111, 222, 331, while no contrast was obtained using 002 and 330 reflections. In planes containing the a^* direction, dark field images with the reflection 900 did not show contrast. It seems, therefore, that in dark field images using reflections which can be described as belonging to the sublattice the microstructures did not appear. On heating *in*



Fig. 9. Bright field image near c -axis showing fringes which are continuous across the twin boundaries (black arrow). Note the defects related to the $27\text{ \AA}$ repeat.

situ up to a furnace temperature of 900°C these microstructures could still be observed.

5. Discussion

Our conclusions concerning the microstructures and transition behaviour of natural kaliophilite are subject to two experimental difficulties. Firstly, in the *in situ* high temperature study of the high-low transition by TEM, the sample temperature was not well constrained. Although a nominal temperature of 900°C was achieved it is certainly possible that the temperature of the sample did not exceed ~ 700°C (Heaney & Veblen, 1990). Secondly, systematic dark field experiments to characterise fully the imaging conditions of the linear defects and the "merohedral twins" were not entirely conclusive. These limitations notwithstanding, the observations do shed considerable new light on the thermal stability of kaliophilite and its possible relationship to other phases of KAlSiO_4 .

The identification of the displacive transition at 725°C, detected by a marked discontinuity in thermal expansion along *c*, implies that two polymorphs exist for kaliophilite. The transition is related to a symmetry change between two hexagonal structures without a change of unit cell. We may postulate that the high temperature phase has space group $P6_322$ and that the low temperature phase is $P6_3$. For the point group symmetry reduction 622 to 6 two diads perpendicular to *c* are lost, allowing the development of merohedral twins. These twins would show only a single orientation of the reciprocal lattice with single diffraction spots, as observed in the TEM study. The twins shown in Fig. 7 could only be imaged when *c* was normal to the film, *i. e.* they showed strong contrast for certain reflections with $l = 0$. A formal analysis of the contrast from merohedral twins requires structure factor informations which is not available in the present case, however. Although the observed twins did not disappear at the nominal furnace temperature of 900°C, it is possible that the sample did not reach the transition temperature of 725°C. For the present, we tentatively suggest that the twins could be transformations twins due to $P6_322 \rightleftharpoons P6_3$ transition, therefore.

The other defects show contrast characteristics similar to antiphase boundaries and appear to be related to the 27 Å superstructure. The hetero-

geneity of the distribution of these defects and the fact that the superstructure reflections persist in single crystal X-ray diffraction patterns collected above 725°C suggest that they are more likely to have originated as mistaken incorporated during crystal growth rather than as a consequence of phase transition, however. They show signs of having a strongly preferred orientation parallel to the *c*-axis (Fig. 8) and less strongly preferred orientations in the a^*b^* plane (Fig. 7). Our preliminary conclusion, therefore, is that they are stacking mistakes in the 27 Å superstructure repeat. These defects, are cut by the merohedral twins, which suggests that they were formed before the twins (Fig. 7). Stacking defects were observed also in high resolution lattice images (Bonaccorsi, 1988).

The *c* dimension of kaliophilite ($c = 8.56$ Å) is smaller than the *c* dimension of kalsilite ($c = 8.69$ Å). The difference may correspond to changes in the framework topology. For example, a dependence of the *c* parameter on the framework topology has been observed in phases of $(\text{Na,K})\text{AlGeO}_4$ (Barbier & Fleet, 1988). The length of the *c* parameter drops from 8.76 to 8.60 Å in the transition from KAlGeO_4 , with kalsilite-like structure (trydimite topology containing UDUDUD rings only) to KAlGeO_4 , with non trydimite topology (containing UDUDUD and UUUDDD rings). A similar dependance is also observed in the $(\text{Na,K})\text{AlSiO}_4$ system: kalsilite contains UDUDUD rings only ($c = 8.69$ Å) while orthorhombic O1- KAlSiO_4 containing UUUDDD and UUDDUD rings, has $c = 8.56$ Å. The marked contrast in the thermal expansion behaviour between kalsilite and O1- KAlSiO_4 is also a reflection of the different framework topologies. Kalsilite has a negative thermal expansion along its *c*-axis (Henderson & Taylor, 1988) whereas, in O1- KAlSiO_4 , *c* expands as temperature increases (Sandomirskiy & Urusov, 1988). The thermal expansion of kaliophilite is thus more like that of O1- KAlSiO_4 than of kalsilite and, taken together, these indirect arguments strongly suggest that kaliophilite does not have a true stuffed tridymite structure as confirmed by Gregorkiewitz (1986). He carried out ion exchange experiments on kaliophilite and observed that Na-exchanged kaliophilite does not assume a nepheline (tridymite-like) topology, but merely it undergoes a decrease in the unit cell volume. The irreversible transition observed above ~ 750°C to a new hexagonal phase with

$a \approx A\sqrt{3}$ and $c \approx C$ probably also involves a change in framework topology.

Acknowledgements: We would like to thank Tony Abraham, Ian Marshall and Ann Graeme-Barber for help during experimentation, Bernd Wruck for DSC analysis and Andy Ridgwell for IR measurements. We are also grateful to M. Pasero and M. Czank for their helpful reviews. D. Cellai thanks the Ministero della Pubblica Istruzione in Italy for the financial support (grants MPI 40 %).

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Received 28 August 1991

Accepted 11 February 1992