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Natural kalsilite, $KAlSiO_4$, with *P*31*c* symmetry: Crystal structure and twinning

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Abstract

A new $KAlSiO_4$ polymorph was found in a granulite facies gneiss from the Punalur district, southern India. The structure was solved and refined on a twinned crystal to an *R* index value of 1.98% for 265 independent reflections. Metamorphic kalsilite is trigonal, space group *P*31*c* with $a = 5.157$ (1) Å, $c = 8.706$ (3) Å, $V = 200.52$ (9) Å^3, $Z = 2$. The overall diffraction symmetry 6/*mmm* exhibited from all the crystals examined arises from a {0001} twinning, related to a mistake in the ordered Al-Si-Al-Si sequence along the *c* axis. The crystal structure is a stuffed derivate of tridymite, and is characterized by six-membered tetrahedral rings with ditrigonal shape. Individual layers of this structure are the same as those of $P6_3$ kalsilite, but are stacked along the *c* axis in an eclipsed manner rather than in the staggered manner of the $P6_3$ structure.

Introduction

At room temperature many structural modifications with a chemical formula close to $KAlSiO_4$ are known. All of them are tectosilicates, with structures consisting of layers of six-membered rings of Al and Si tetrahedra and K^+ located in the large cavity. Three-dimensional connectivity is assured by apical O atoms of the tetrahedra that point up (U) and down (D) to link adjacent layers. At least three different framework topologies are known for the $KAlSiO_4$ phases. The high tridymite-like topology, characterized by UDUDUD rings, is found in natural and synthetic hexagonal kalsilite (Perrotta and Smith 1965; Dollase and Freeborn 1977), and in the structure of other related minerals like panunzite (Merlino et al. 1985) and trikalsilite (Bonaccorsi et al. 1988). A different framework topology is found in the structure of "O1-$KAlSiO_4$" and is based on two different ring configurations, UUDDUD and UUUDDD (Gregorkiewitz and Schäfer 1980). Finally, UUUDDD rings characterize the structure of the *Icmm* $KAlSiO_4$ phase (Minor et al. 1978).

Kaliophilite is the other $KAlSiO_4$ phase that occurs in nature. Despite having a unit cell closely related to those of kalsilite, the evidence from conductivity and exchange experiments (Gregorkiewitz 1986) and thermal behavior (Cellai et al. 1992) suggests that it does not have a tridymite framework topology.

Natural kalsilite occurs mainly in K-rich, silica-undersatured volcanic rocks, but it is also found (rarely) in metamorphic rocks. The first structure refinement was carried out by Perrotta and Smith (1965) on a crystal of volcanic kalsilite with Na:K ≈ 0.02:0.98 in the space group $P6_3$. In this structure, Al and Si are distributed orderly over alternating tetrahedra, and the six-membered rings are ditrigonally distorted with opposite rotations on adjacent layers so that the basal O atoms form a tricapped trigonal antiprism around the K ion. The apical O was found to be displaced by 0.25 Å from the threefold axis and therefore statistically distributed over three sites, giving Al-O-Si angles <180°. Synthetic kalsilite was produced from nepheline by ion exchange in molten KCl by Dollase and Freeborn (1977). At room temperature such crystals show intensities of the *hhl*, l = odd reflections different from crystal to crystal, with diffraction symmetry appearing to range continuously from that of space group $P6_3$ to $P6_3mc$. Dollase and Freeborn (1977) performed a structure refinement in space group $P6_3mc$, using a crystal with *hhl*, l = odd reflections absent. The structure is quite similar to that of natural kalsilite, but, in addition, the basal O atom was found to be disordered between two mirror-equivalent sites producing an average structure of symmetry $P6_3mc$ that corresponds to the superposition of positive and negative ditrigonal distortions. According to Dollase and Freeborn (1977) this form can be considered as the average structure of $(11\bar{2}0)$ mirror-related $P6_3$ domains. The domains are considered to be in a twin relationship, but with a size small enough to diffract X-rays coherently (*hhl* reflections systematically absent). A similar domain structure leading to apparent $P6_3mc$ symmetry was also reported by Andou and Kawahara (1984) for synthetic kalsilite prepared by hydrothermal methods. By analogy with twinning in low quartz, Andou and Kawahara (1982) suggested that such a domain structure in kalsilite can be ascribed to the displacive high ($P6_3mc$) → low ($P6_3$) transition that they observed at 875 °C when the *hhl*, with l=odd reflections disappeared from their X-ray powder diffraction pattern. Later, Kawahara et al. (1987) determined the structure of the $P6_3mc$ form using X-ray diffraction data collected from a crystal held at 950 °C. In addition, the same authors speculated on the existence of a disordered high kalsilite, with $P6_3/mmc$ symmetry.

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TABLE 1. Crystal data and experimental details for metamorphic kalsilite

Crystal system	trigonal
Space group	*P*31*c*
Cell parameters	
a(Å)	5.157(1)
b(Å)	5.157(1)
c(Å)	8.706(3)
V(Å^3)	200.52(9)
Formula units per unit cell, *Z*	2
Diffractometer	Enraf Nonius CAD4
Radiation	Mo*K*α (0.71069 Å)
Crystal size (μm)	60 × 90 × 150
Scan mode	ω-2θ
Scan width (°)	2.00 (ω)
Scan speed (°/min)	3.2 (ω)
Theta range (°)	$2 < \theta < 35$
Range of *hkl*	−8,8 −8,8 0,14
R_{symm}(%) (Laue $\bar{3}1m$)	4.85
Independent refl.	313
N_{obs}	265
Refined parameters	22
R_{obs} (%)	1.89
R_{all} (%)	2.43

Notes: $R_{symm} = \Sigma|F^2_o - F^2_o|/\Sigma F^2_o$; N_{obs} = number of reflections with $F_o > 4\sigma_{F_o}$; $R_{obs} = \Sigma|F_o - F_c|/|F_o|$.

Capobianco and Carpenter (1989) observed that kalsilite crystals from metamorphic rocks of the Punalur district (Southern India) show weak *hhl, l* = odd reflections. On the basis of XRD and TEM investigations on the same sample, Carpenter and Cellai (1996) suggested that this kalsilite consists of an intergrowth of $P6_3$ and *P*31*c* structures having the same unit cell and sharing the (0001) plane. The ratio between $P6_3$ and *P*31*c* phases varied widely on an electron optical scale from more than ~90:10 through ~50:50 to less than ~10:90.

The aims of the present paper are to present the results of a structure refinement of *P*31*c* metamorphic kalsilite and then to consider its structural relationship to hexagonal kalsilite.

EXPERIMENTAL AND STRUCTURE SOLUTION

A crystal of kalsilite was separated from a granulite facies gneiss from the Punalur district in Kerala, southern India, kindly provided by M. Santosh (Centre for Earth Sciences Studies, Akkalum, Trivandrum, India). Peak metamorphic conditions for the Punalur assemblages (kalsilite, leucite, hibonite, spinel, corundum, titanite, perovskite, Ti-bearing phlogopite, and potassium feldspar) have been estimated as 700–800 °C and 3.5–6.5 kbars (Sandiford and Santosh 1991). This kalsilite is essentially end-member $KAlSiO_4$ (Capobianco and Carpenter 1989; Sandiford and Santosh 1991) with the K/Na molar ratio close to 350 (Capobianco and Carpenter 1989).

Lattice parameters were determined by means of the least-squares method using 25 high-θ reflections measured with a CAD4 single-crystal diffractometer (see Table 1). The crystal exhibited overall diffraction symmetry 6/*mmm,* and *hhl, l* = odd reflections were systematically absent. However, very weak 111 and 113 reflections were detected, indicating that a small portion of $P6_3$ phase is probably present, in agreement with the result of TEM investigations (Carpenter and Cellai 1996). No other extra reflections or diffuse reflections were observed. Intensity data were collected and subsequently corrected for Lorentz and polarization factors and for absorption (North et al. 1968).

An attempt to refine the crystal structure in space group $P6_3mc$ was undertaken starting with the positional parameters published by Dollase and Freeborn (1977) for synthetic $P6_3mc$ kalsilite. The R_{symm} value was 4.94% (Laue symmetry 6/*mmm*) and the refinement converged to a final *R* of 6.8% for 198 observed reflections with $F_o > 4\sigma_{F_o}$. This refinement gave a disordered model for O atoms quite similar to that proposed by Dollase and Freeborn (1977). A refinement was also carried out with O2 located on the triad axis, but the *R* index did not improve significantly. However, an ordered model for the O atoms is possible if the *P*31*c* subgroup symmetry is taken into account. Therefore, the refinement was continued in space group *P*31*c*. The R_{symm} value in the $\bar{3}1m$ Laue group was 4.85%. Convergence was rapidly obtained to a final *R* index of 2.43% for 265 observed reflections, and *R* = 2.99% for all 313 reflections. The Δ*F* map did not show evidence for split O atoms. However, the shape of the thermal ellipsoid of O2 might be interpreted in terms of a split-atom model. A further refinement was therefore attempted with O2 displaced from the threefold axis. This refinement converged to a final *R* of 2.45%, with *R* = 3.06% for all 313 reflections. In both these refinements values greater than 0.80 occurred in the correlation matrix for the pair z_{Si} - z_{Al}, and a careful examination of the refined parameters revealed that the structural model obtained is consistent with the higher symmetry of the $P\bar{6}2c$ space group. On the other hand, this higher symmetry would require a completely disordered distribution for Si and Al between the tetrahedral sites, which is most unlikely. Therefore, it was assumed that the apparent $P\bar{6}2c$ symmetry arises from the presence of {0001} twinning in crystals of *P*31*c* symmetry. If such twinning occurs, all *hkl* reflections of the first twin component are superimposed on the $hk\bar{l}$ reflections from the second component. The structure refinement, performed by means SHELXL93 (Sheldrick 1993), was then continued following the method of Pratt et al. (1971) for twinned structures. The refined value of the fraction of the first twin component was 0.55, which accounts very well for the relatively low value (4.94%) of R_{symm} in the 6/*mmm* Laue group. The final *R* value was 1.98% for 265 observed reflections and 2.43% for all 313 data. An attempt to refine the structure with the O2 atom displaced off the triad axis gave similar values for *R* indices but unreliable bond distances for the Si and Al tetrahedra. The model with O2 on the triad axis was therefore adopted. It remains highly probable, however, that the strong anisotropy of the O2 thermal ellipsoid corresponds to the positional uncertainty of O2 in the *a-b* plane. If this is the case, the straight intersheet T1-O2-T2 angle is as an artifact resulting from the statistical disorder of the O2 position.

TABLE 2. Fractional atomic coordinates and isotropic and anisotropic displacement parameters (Å^2) of $P31c$ kalsilite

Atom	x	y	z	U_{eq}	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
K	0	0	¼*	0.0165(3)	0.0154(3)	U_{11}	0.0187(5)	0	0	$U_{11}/2$
T1	⅓	⅔	0.0594(4)	0.0046(5)	0.0013(7)	U_{11}	0.0112(8)	0	0	$U_{11}/2$
T2	⅓	⅔	0.4416(4)	0.0089(6)	0.0104(9)	U_{11}	0.0058(6)	0	0	$U_{11}/2$
O1	0.616(1)	0.011(2)	0.000(1)	0.0170(5)	0.009(1)	0.009(1)	0.031(1)	0.004(1)	0.006(1)	0.003(1)
O2	⅓	⅔	0.260(1)	0.025(1)	0.036(1)	U_{11}	0.004(2)	0	0	$U_{11}/2$

Note: The form of the anisotropic displacement factor is exp $[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2hka^*b^*U_{12} + 2hla^*c^*U_{13} + 2klb^*c^*U_{23})]$.
* Fixed during refinement.

Scattering curves for neutral atoms were taken from *International Tables for X-ray Crystallography* volume IV (Ibers and Hamilton 1974). Experimental details are reported in Table 1. The final atomic coordinates and displacement parameters are given in Table 2.

DESCRIPTION OF THE STRUCTURE

As in the structure of $P6_3$ kalsilite (Perrotta and Smith 1965), the tetrahedral framework of $P31c$ kalsilite has the tridymite topology with UDUDUD rings that are stacked along the c axis and linked via the O2 O atoms (Fig. 1). The rings have ditrigonal shape in both structures, and the difference between the $P6_3$ and $P31c$ structures is in the conformation between adjacent layers. In $P31c$ kalsilite, successive layers are stacked in an "eclipsed" conformation of the O_3T1-O2-T2O_3 groups that connect the layers; thus ditrigonal rings in succeeding layers point in the same directions (Fig. 1). In $P6_3$ kalsilite, succeeding layers are stacked in a "staggered" conformation such that ditrigonal rings point in opposite directions. In this respect, the $P31c$ structure of kalsilite is isostructural with the $P31c$ phases of $KLiSO_4$ (Zhang et al. 1988) and $RbLiCrO_4$ (Makarova et al. 1993). Eclipsed conformations were also reported for nepheline (Buerger et al. 1954), trikalsilite (Bonaccorsi et al. 1988), and panunzite (i.e., natural tetrakalsilite; Merlino et al. 1985) in the system nepheline-kalsilite.

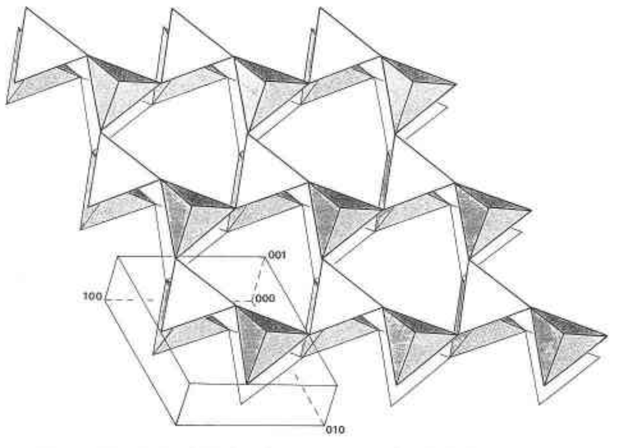

FIGURE 1. Crystal structure of kalsilite with $P31c$ symmetry showing tetrahedral layers perpendicular to c. Shaded and empty tetrahedra represent T1 and T2, respectively. K atoms are not shown.

The interatomic distances and angles for $P31c$ kalsilite are listed in Table 3. The K^+ cation is coordinated to nine O atoms located at the vertices of a tricapped trigonal prism, whereas in $P6_3$ kalsilite the coordination polyhedron for K^+ is a tricapped trigonal antiprism because of the staggered configuration of the tetrahedral layers. However, the mean ⟨K-O⟩ distance (2.968 Å) is quite similar to those obtained for hexagonal kalsilite (⟨K-O⟩ = 2.97 Å Perrotta and Smith 1965; ⟨K-O⟩ = 2.92 Å Andou and Kawahara 1984). The mean bond lengths are 1.727 Å for T1-O and 1.618 Å for T2-O. Comparison of these distances with those found in typical framework silicates suggests complete ordering of Si and Al. [The mean ⟨T-O⟩ distances found in related structures, where Al and Si atoms are completely ordered, are: ⟨Al-O⟩ = 1.744(29), 1.724(45), 1.740(29) Å, and ⟨Si-O⟩ = 1.611(27), 1.613(32), 1.616(29) Å for hexagonal kalsilite (Perrotta and Smith 1965), trikalsilite (Bonaccorsi et al. 1988) and panunzite (Merlino et al. 1985), respectively]. Disordering of Si-Al in similar structures has been reported in nepheline (Dollase and Peacor 1971) and in hexagonal kalsilite (Andou and Kawahara 1984) on the basis of the T-O distances. The electrostatic valance balance calculated according to the method of Brese and O'Keeffe (1991) is shown in Table 4, and the results are fairly satisfactory for both O atoms.

CONCLUSIONS

Natural metamorphic kalsilite has $P31c$ symmetry and complete Al-Si order. The strong $6/mmm$ pseudosymmetry observed in all crystals examined during this study is evidently related to the presence of twin domains with proportions close to 50%. It means that many twin bound-

TABLE 3. Selected bond lengths (Å) and bond angles (°) for $P31c$ kalsilite

K-O1 × 3	2.962(9)
K-O1 × 3	2.962(9)
K-O2 × 3	2.979(8)
Average value	2.968
T1-O1 × 3	1.720(7)
T1-O2	1.746(9)
Average value	1.727
T2-O1 × 3	1.630(8)
T2-O2	1.581(9)
Average value	1.618
T1-O1-T2	140.2(4)
T1-O2-T2	180.0

TABLE 4. Valence balance for *P*31*c* kalsilite

	T1	T2	K	Σ
O1 × 3	0.763 × 3	0.966 × 3	0.113 × 3 0.113 × 3	1.96 × 3
O2	0.711	1.102	0.107 × 3	2.13
Σ	3.00	4.00	1.00	8.00

aries occur randomly within the crystals, so that both orientations are equally represented. The twin-boundary can be seen as a mirror plane parallel to (0001) at z = ¼ and z = ¾ that arises from a mistake in the ordered Si-Al-Si-Al sequence of tetrahedral sites along the *c* axis. Given that the proportion of twins is close to 50:50, it seems likely that they developed as a consequence of a phase transition from a higher symmetry structure.

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