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X-ray study of the trigonal → hexagonal phase transition in metamorphic kalsilite

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ABSTRACT

High-temperature annealing experiments on metamorphic kalsilite ($KAlSiO_4$) indicate that there is an irreversible phase transition from the $P31c$ to $P6_3$ structure at ~200 °C. Powder X-ray investigations indicate that the transformation is incomplete. The proportion of $P6_3$ phase increases as a function of temperature, attaining 70% for the powdered sample at ~500 °C. At higher temperatures, the fraction of sample transforming to $P6_3$ phase seems to be independent of temperature, and probably depends on the structural state of the starting material as influenced by mechanical grinding. Transformation proceeds by tetrahedral rotation such that successive (001) sheets undergo opposite-sense rotations. The transition behavior differs for single crystals, which had not been mechanically ground; at 500 °C single crystals transformed completely into the $P6_3$ phase. Single-crystal structure refinements of the $P6_3$ phase indicate that the structure is similar to that of volcanic kalsilite. Both apical and basal O atoms show large anisotropic displacement parameters, but the displacement of the apical oxygen does not exhibit the trigonal distribution that has been observed in volcanic kalsilite. The more pronounced positional disorder in volcanic kalsilite is due to the presence of sodium.

INTRODUCTION

The rock-forming feldspathoid kalsilite ($KAlSiO_4$) occurs mainly in K-rich silica undersaturated volcanic rocks, and in metamorphic rocks. The first structure refinement by Perrotta and Smith (1965) on a crystal of volcanic kalsilite with Na:K ~0.02:0.98 gave the space group $P6_3$ (low kalsilite). The structure (Fig. 1) is characterized by AlO_4 and SiO_4 tetrahedra forming an ordered three dimensional framework which consists of six-membered rings of tetrahedra pointing alternately up (U) and down (D) (tridymite framework topology UDUDUD). All rings are ditrigonally distorted, and are stacked along the *c* direction, joined via the apical O atoms in a staggered configuration, which means that all ditrigonal rings in one sheet point in one direction and all the rings in the next sheet point in the opposite direction. The apical oxygen was found to be displaced by 0.25 Å from the threefold axis and appears to be randomly distributed among three sites, giving intersheet Al-O-Si bond angles <180°. However the X-ray refinement of Perrotta and Smith ended up with a large R value ($R = 5.9\%$) which is not uncommon in the structures of the kalsilite-nepheline series $(K,Na)AlSiO_4$. Cellai et al. (1997) determined the crystal structure of Na-free metamorphic kalsilite on a twinned crystal. Their refinement converged to a final R-value of 1.98% and showed that the structure has $P31c$ symmetry. A difference Fourier map did not show evidence for splitting of the apical oxygen position, and a model with the apical oxygen on the triad axis was therefore adopted. However, the strong anisotropy of the thermal ellipsoid of the apical oxygen could result from some kind of disorder (static or dynamic) of the oxygen, and the apparent intersheet Al-O-Si bond angle of 180° is probably not real. Individual sheets of $P31c$ kalsilite are essentially the same as those of the $P6_3$ structure but are stacked in an eclipsed manner, so that ditrigonal rings in succeding sheets point in the same directions. $P31c$ kalsilite is isotypic with the $P31c$ phase of $KLiSO_4$ (Bansal et al. 1980; Zhang et al. 1988; Rajagopal et al. 1991; Bhakay-Tamhane et al. 1985, 1991) and $RbLiCrO_4$ (Makarova et al. 1993). By studying the change in intensities of *hhl* reflections in metamorphic kalsilite, an irreversibile structural phase transition involving the symmetry change $P31c \rightarrow P6_3$ on heating from room temperature was proposed by Carpenter and Cellai (1996).

Synthetic kalsilite produced from nepheline by K-exchange (Dollase and Freeborn 1977) showed intensities of the *hhl*, l = odd reflections differing from crystal to crystal. Dollase and Freeborn performed a structure refinement in space group $P6_3mc$ using a crystal with *hhl*, l = odd reflections absent. Their structure is quite similar to $P6_3$ kalsilite; but, in addition, the basal O atoms are disordered between two mirror equivalent sites producing an average $P6_3mc$ structure. They pointed out that $(11\bar{2}0)$ mirror-related $P6_3$ domains generate overall $P6_3mc$ symmetry. A similar domain structure was also reported for synthetic kalsilite prepared by hydrothermal methods (Andou and Kawahara 1984). Xu and Veblen (1996) found that kalsilite crystals prepared from nepheline by K-exchange are structurally complex, and, in particular, Na-poor and Na-free kalsilite crystals are composed of (0001) domains with $P6_3$ and $P31c$ symmetries.

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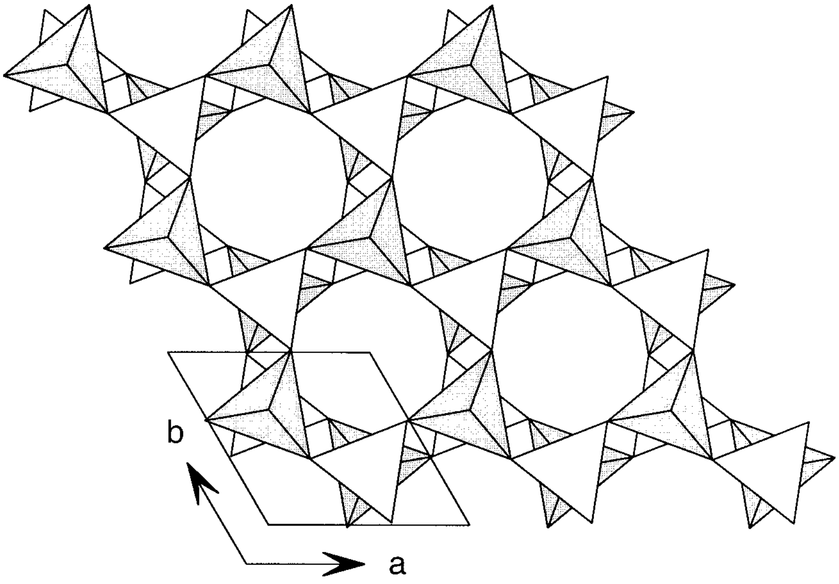

FIGURE 1. Crystal structure of kalsilite with $P6_3$ symmetry showing tetrahedral layers perpendicular to **c**. Shaded and empty tetrahedra represent Al and Si tetrahedra, respectively. K atoms are not shown.

Synthetic kalsilite has $P6_3mc$ symmetry at 950 °C with open hexagonal rings (high kalsilite; Kawahara et al. 1987). A reversible symmetry change $P6_3 \leftrightarrow P6_3mc$ at high temperature was proposed for synthetic and natural sample (Andou and Kawahara 1982; Abbott 1984; Kawahara et al. 1987; Capobianco and Carpenter 1989; Carpenter and Cellai 1996). The transition occurs by means of an intermediate superstructure, which coexists with low kalsilite between 850 and 920 °C (Capobianco and Carpenter 1989; Carpenter and Cellai 1996). High kalsilite has apparently complete Si-Al order, though there is some speculation (Kawahara et al. 1987; Abbott 1984) that, at higher temperatures, the symmetry become $P6_3/mmc$ as a result of Al-Si disordering. Above >1000 °C, kalsilite transforms irreversibily to the O1-$KAlSiO_4$ phase (Tuttle and Smith 1958) with a different topology than tridymite, based on two different ring configurations UUDDUD and UUUDDD (Gregorkiewitz and Schäfer 1980; Merlino 1984).

Na-bearing volcanic kalsilite contains weak and diffuse superstructure reflections indicating a supercell in which $a_{super} = \sqrt{3}\,a_{sub}$ and a_{super} is rotated 30° about the c axis relative to a_{sub} (Smith and Sahama 1957; Perrotta and Smith 1965; Carpenter and Cellai 1996; Xu and Veblen 1996). Smith and Sahama (1957) reported that annealing at 600 °C for 3d caused the extra reflections to disappear. Carpenter and Cellai (1996) pointed out that all crystals with compositions in the range Ks_{88-97} give electron diffraction patterns at room temperature containing the superstructure reflections, including Ks_{88} that has been annealed at 950 °C. They found variations in the intensities of these reflections, and probably the most diffuse reflections might be overlooked in single-crystal X-ray diffraction patterns. The experiments of Xu and Veblen (1996) revealed that annealing at high temperature causes the superstructure reflections to become weaker; a sample annealed at 900 °C revealed only continuous streaking in the positions previously occupied by superstructure reflections in the c^*-[0110]* SAED pattern, which may indicate the loss of periodicity within and therefore small size of the superstructure domains. Kaliophilite is another phase with composition in the range $Ne_{19}Ks_{81}$ to ~ Ne_0Ks_{100} (Barbieri et al. 1970) where Ne and Ks refer to $NaAlSiO_4$ and $KAlSiO_4$ components. It has a large unit cell closely related to that of kalsilite, but its microstructure, thermal behavior, ionic conductivity and exchange properties (Cellai et al. 1992; Gregorkiewitz 1986) suggest that it does not have a tridymite topology.

The present study was undertaken to refine the crystal structure of the $P6_3$ phase of metamorphic kalsilite and determine its relationship with $P6_3$ volcanic kalsilite. Anneal and quench experiments provide new insights into the nature of the $P31c \rightarrow P6_3$ phase transition.

EXPERIMENTAL DETAILS

Starting material

Metamorphic kalsilite was separated from a sample of a granulite facies gneiss from the Punalur discrict in Kerala, southern India, which was kindly provided by M. Santosh Centre of Earth Science Studies, Akkalum, Trivandrum, India. This kalsilite is essentially end-member $KAlSiO_4$, with only ~0.002 Na^+ ions per K^+ ion and an equivalent proportion of Fe substituted for Al (Capobianco and Carpenter 1989; Sandiford and Santosh 1991). Peak metamorphic conditions for the Punalur assemblages (kalsilite, leucite, hibonite, spinel, corundum, sphene, perovskite, Ti-bearing phlogopite, and potassium feldspar) have been estimated to be 700–800 °C and 3.5–6.5 kbar (Sandiford and Santosh 1991).

Annealing experiments assessed by X-ray powder diffraction

The irreversible $P31c \rightarrow P6_3$ phase transition in kalsilite can be detected as a change in the intensities of the *hhl* reflections. Those with l = even would be expected to decrease in intensity, whereas those with l =odd should increase (all reflections with hhl, l = odd are systematically extinct in space group $P31c$). The 111 and 112 reflections were selected for systematic study. Separated kalsilite crystals were crushed with a mortar and pestle and the resulting powders were annealed in a platinum crucible held for 1 h in a resistance furnace, at different temperatures between 100 and 1000 °C, and then quenched in air. In addition, at 240 and 500 °C, annealing experiments were also performed for 1 h, 1 d, and 4 d. The annealed powders were mounted in a glass capillaries of 0.3 mm width which were rotated during the X-ray measurements. X-ray powder intensity data were collected on a STOE (STADI P) powder diffractometer with Debye-Scherrer geometry, using a focusing germanium (111) monochromator and Cu$K\alpha_1$ radiation, $35° < 2\theta < 41°$, a PSD (Photo Sensitive Detector)-step width of 0.05°, a PSD-channel width of 0.02°, and a measuring time of 10 s/step. The proportion of $P6_3$ and $P31c$ phases was estimated for each powder by measuring the intensities of the 111 and 112 reflections. The amount of transformed material varied with annealing temperature but was independent of annealing time at 240 and 500 °C.

X-ray powder data were also collected in the range $15° < 2\theta < 80°$ for the untreated sample and for a sample annealed at 950 °C for 1 h (Fig. 2). A structure refinement was carried out using the β-version of the Rietveld analysis program RIETAN 97 (Izumi 1993). For the untreated sample the best fit of the observed intensities was obtained with a mixture of two phases: 93% $P31c$ and 7% $P6_3$. During the refinement 39 parameters were varied in total: the zero-point of the counter, 12 background parameters, 6 profile parameters, the scale factor for both phases, 10 atomic and 2 metric parameters for the $P31c$ phase and 4 atomic and 2 metric parameters for the $P6_3$ phase. The final residuals for the pattern, the structure factors and the lattice parameters are: $R_{wp} = 0.094$, $R_p = 0.069$; $R_F = 0.010$, $a = 5.1596(2)$, $c = 8.7169(3)$ Å, $V = 200.94(1)$ Å^3 for the $P31c$ structure; $R_f = 0.010$, $a = 5.162(2)$ Å, $c = 8.710(4)$ Å, $V = 201.0(1)$ Å^3 for the $P6_3$ structure. The annealed sample contained only the $P6_3$ phase and the final residuals for the pattern, the structure factors, and the lattice parameters are $R_{wp} = 0.048$, $R_p = 0.037$, $R_f = 0.013$, and a = 5.16323(8) Å, c = 8.7096(1) Å^3, V = 201.081(5) Å. Here, 33 parameters were refined: the zero point, the scale factor, 12 background and 6 profile parameters, 2 lattice parameters, and 11 atomic parameters.

Single-crystal X-ray diffraction

Data collection parameters and cell parameters are in Table 1. The first data collection was carried out on a crystal of kalsilite that was annealed at 500 °C for 4 days and quenched in air. The measured intensities of the 111 and 112 reflections indi-

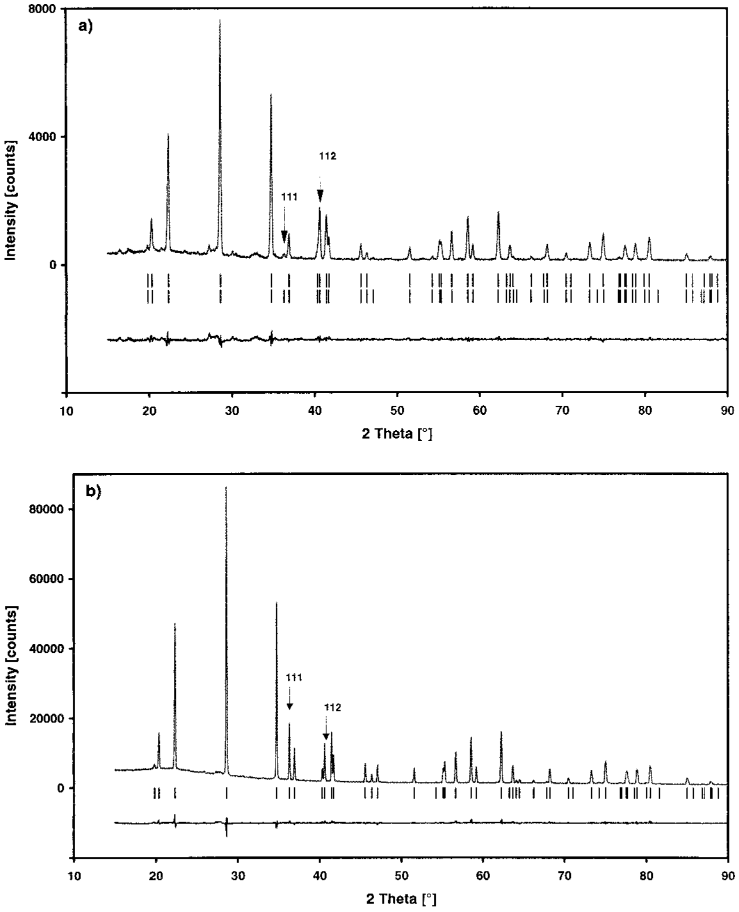

FIGURE 2. X-ray powder diagram of kalsilite. (**a**) Starting material containing a mixture of two phases: 93% $P31c$ phase and 7% $P6_3$ phase. (**b**) Sample annealed at 950 °C for 1 h consisting of 100% $P6_3$ phase. From top to bottom of each frame the measured pattern, the peak positions and the calculated intensities are shown.

TABLE 1. Crystal data of hexagonal metamorphic kalsilite, $KAlSiO_4$ at room temperature, and experimental details for single-crystal structure refinement

Crystal system	hexagonal	2 θ range (°)	3.8 < 2θ < 56.3
Space group	$P6_3$	Range of *hkl*	–6,6; –6,6; –11,11
a (Å)	5.1627(7)	*R*(int) (%)	3.87
c (Å)	8.706(2)	No. of independent reflections	335
V (Å^3)	200.98(8)	N_{obs} ($F_0>4\sigma_{F_O}$)	245
Formula units per unit cell, Z	2	No. of refined parameters	22
Diffractometer	STOE IPDS	R_{obs} (%)	2.13
Radiation	Mo*K*α (0.71073 Å)	R_{all} (%)	3.60

cated that the crystal had not been transformed completely to the $P6_3$ phase. The same crystal was therefore annealed again at the same temperature for two weeks. Analysis of the intensities indicated that the crystal had now transformed completely to the $P6_3$ phase. The structure was refined using the positional parameters of $P6_3$ volcanic kalsilite published by Perrotta and Smith (1965). An ordered arrangement of tetrahedral Si and Al atoms was assumed initially and later confirmed during the refinement. Using 245 observed reflections ($F_o > 4\sigma_{F_o}$), a least squares refinement using the program SHELXL93 (Sheldrick 1993) was carried out with anisotropic displacement parameters for all atoms, converging to a final *R* value of 2.13%. Final atomic positions, equivalent isotropic displacements parameters, and anisotropic displacement parameters are given in Tables 2 and 3. Selected bond lengths and bond angles are given in Table 4. A difference-Fourier map did not show evidence for residual electron density at the off-axis positions of the apical oxygen as observed in volcanic kalsilite (Perrotta and Smith 1965). However, the large anisotropic displacement parameter of the apical oxygen indicates a strong positional disorder. An attempt to refine the structure with the O1 atom displaced off the triad axis gave similar *R* values, and the model with O1 on the threefold axis was adopted for comparison with *P*31c kalsilite. A possible explanation for the off-axis position of O1 in volcanic $P6_3$ kalsilite is given later.

TABLE 2. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for single crystal refinement of $P6_3$ metamorphic kalsilite

Atom	x	y	z	U_{eq}
K	0	0	0.25*	0.0181(3)
Al	1/3	2/3	0.443(1)	0.0094(4)
Si	1/3	2/3	0.061(1)	0.0076(7)
O1	1/3	2/3	0.241(3)	0.036(2)
O2	0.6027(5)	0.0119(5)	0.997(1)	0.0198(5)

*Fixed during refinements.

TABLE 3. Anisotropic displacements parameters (Å^2) of metamorphic $P6_3$ kalsilite

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
K	0.0174(3)	U_{11}	0.0194(7)	0	0	$U_{11}/2$
Al	0.0086(6)	U_{11}	0.011(2)	0	0	$U_{11}/2$
Si	0.0081(7)	U_{11}	0.007(2)	0	0	$U_{11}/2$
O1	0.052(1)	U_{11}	0.005(5)	0	0	$U_{11}/2$
O2	0.011(1)	0.012(1)	0.036(1)	0.002(1)	0.003(1)	0.006(1)

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

TABLE 4. Selected bond lenghts (Å) and bond angles (°) for metamorphic $P6_3$ kalsilite

K-O2 ×3	2.951(9)	Si-O2 ×3	1.624(2)
K-O2 ×3	2.989(9)	Si-O1	1.59(1)
K-O1 ×3	2.981(8)		
		Al-O1-Si	180.0
Al-O2 ×3	1.724(3)	Al-O2-Si	140.8(1)
Al-O1	1.74(1)		

RESULTS AND DISCUSSION

The $P6_3$ structure

The structure of $P6_3$ kalsilite viewed along the **c** axis is shown in Figure 1. The structure is a stuffed derivate of the high-tridymite framework. Tetrahedra are corner linked to form sheets normal to the **c** axis. These sheets are connected to form a 3-D framework by sharing the O1 atom. Two independent tetrahedra exist occupied by Si^{4+} and the other by Al^{3+}. This framework encloses one crystallographically distinct cavity, which is occupied by K^+. The coordination polyhedron of potassium, which lies on the midplane between adjacent tetrahedral sheets, consists of six O2 atoms arranged to form a trigonal antiprism plus three O1 atoms so that a total of nine nearly equidistant O atoms results (Table 4).

The O atoms of the $P6_3$ structure show strong anisotropic displacement parameters (Table 3). The electron density of the apical O1 atom is spread out mainly in the (001) plane, whereas the density for the basal O2 atom is elongated along [001]. This picture is consistent with the AlO_4 and SiO_4 tetrahedra having some kind of positional disorder, either by dynamic oscillations or static tilts out of the (001) plane. The displacement anisotropy is similar to that of *P*31*c* kalsilite, but the mean-square amplitude for O1 oxygen in the $P6_3$ structure is greater than in the *P*31*c* structure. These larger anisotropic displacements correlate with the trend observed for the *c* parameters of the hexagonal unit cell, showing that the shorter *c* axis of the $P6_3$ structure results from a more pronounced tilting of its tetrahedral framework (c = 8.7096(1) Å; c = 8.7169(1) Å for $P6_3$ and *P*31*c* powder structure refinements, respectively). However, neither the *P*31*c* nor the $P6_3$ structure of metamorphic kalsilite showed the splitted O1 atom, which has been reported for volcanic $P6_3$ kalsilite (Perrotta and Smith 1965; c = 8.69 Å) which always contains some sodium. A sodium atom on the K^+ site is under-bonded and tends to draw some of the oxygen neighbors closer to it. Collapse around Na atom could therefore be responsible for the splitting of O1 atom on three positions around the ternary axis. Monte Carlo simulations (Welberry and Glazer 1994) performed on the $P6_3$ phase of $KLiSO_4$ explain the splitting of the apical oxygen with a potassium-deficient model. In this model a small percentage of po-

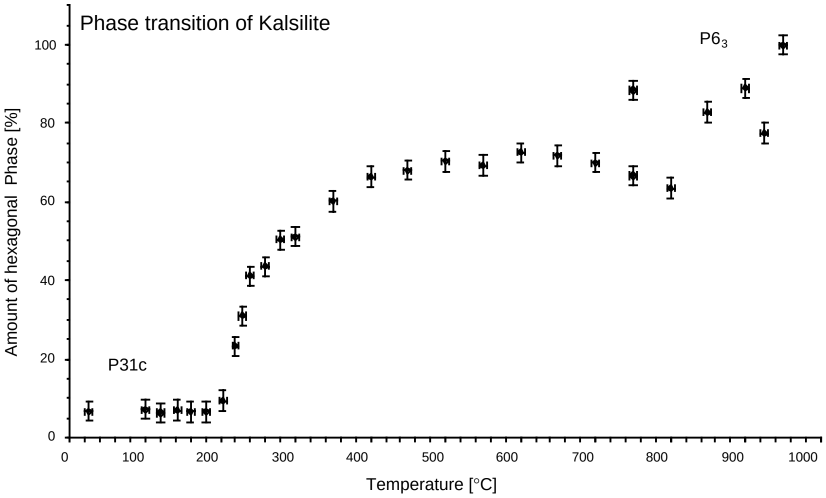

FIGURE 3. Amount of hexagonal phase as a function of annealing temperature for powdered kalsilite. Each sample was annealed for 1 h and then quenched in air.

tassium sites are occupied by lithium (5%), which is highly under-bonded and needs to draw O atoms toward it. The results of the simulations suggest a splitted distribution of the O1 atoms on three sites around the ternary axis, in agreement with the observation. Apparently, the splitting of O1 is related to the supercell ($a_{super} = \sqrt{3}\, a_{sub}$) of volcanic kalsilite, where diffuse extra reflections are always observed (Perrotta and Smith 1965; Carpenter and Cellai 1996; Xu and Veblen 1996). Diffuse extra reflections are not observed in metamorphic kalsilite (Carpenter and Cellai 1996) in accordance to the absence of Na atoms.

The Si-O1 distance of 1.59 Å is rather short; and the Si-O1-Al angle is formally 180°. The highly anisotropic displacement parameters of the O1 atom clearly indicate positional disorder with violation around the threefold symmetry axis, and the real Si-O distances must be larger, as reported for other compounds with symmetry-restricted groups forcing straight Al-O-Si bonds (Liebau 1985).

The trigonal → hexagonal phase transition

The 111 reflection was found to be very weak and broad in patterns from both untreated kalsilite and kalsilite annealed below 200 °C, indicating that a small amount of $P6_3$ structure is present. TEM observations (Carpenter and Cellai 1996) and single-crystal X-ray structure refinement (Cellai et al. 1997) revealed that the $P31c$ structure is twinned and that a twin boundary is a unit of $P6_3$ structure. The intensity of the 111 reflection increases rapidly for samples annealed above 200 °C, indicating that significant structural changes must have occurred during this irreversible change. The accompanying reduction in intensity $I(112)$, shows that the $P31$c structure is converting to the $P6_3$ structure (Fig. 3). The $P31c \rightarrow P6_3$ phase transition in mechanically ground samples is characterized by a large temperature interval where both phases coexist. Similar behavior is shown by the $P31c \leftrightarrow P6_3$ transition in $KLiSO_4$ (Bhakay-Tamhane et al. 1991; Perpetuo et al. 1992). The increase of the proportion of the $P6_3$ phase is a function of annealing temperature between ~200 and ~500 °C. Above ~500–600 °C the amount of transformed phase does not increase, and at higher temperature (>700 °C) the amount of transformed phase is independent of the annealing temperature. Probably at high temperatures the transformation behaviour depends on the starting material, i.e., on sample preparation. Crystals containing the $P6_3$ phase without a detectible proportion of $P31c$ have been obtained only in samples annealed at 950 °C. Single crystals of kalsilite displayed a different transition behaviour, with a smaller temperature interval of coexistence for the two phases (Carpenter and Cellai 1996). The effect of grinding have influence on the transition behaviour also in tridymite (Cellai et al. 1995).

With regard to the driving forces for the $P31c \rightarrow P6_3$ phase transition, only one process should be taken into account: the displacement of the basal O atoms. The two structures differ only in the ordering scheme of their basal O atoms atoms. In the $P31c$ structure the six-membered rings have identical configurations in successive sheets (eclipsed configuration), whereas in the $P6_3$ structure, succeeding sheets are stacked in a staggered configuration such that the six-membered rings point in opposite directions. In the $P31c$ structure, the normal stacking of sheets is interrupted along a (001) twin boundary producing two successive sheets having the opposite sense of rotation and this corresponds to the $P6_3$ structure (Carpenter and Cellai 1996). Reorganisation of the $P31c$ structure to the $P6_3$ could be accomplished by simple rotation (around the ternary axis) of the tetrahedra in every second sheet starting in the vicinity of the (001) twin boundaries where the adjoining regions are already rotated.

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