Phase stability, elastic behavior, and pressure-induced structural evolution of kalsilite: A ceramic material and high-T/high-P mineral

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ABSTRACT

The phase stability, elastic behavior, and pressure-induced structural evolution of a natural metamorphic kalsilite (ideal formula KAlSiO₄) from Punalur (Kerala district in southern India), with P31c symmetry and a K/Na molar ratio of ~350, has been investigated by in situ X-ray single-crystal diffraction up to ~7 GPa with a diamond-anvil cell under hydrostatic conditions. At high-pressure, a previously unreported iso-symmetric first-order phase transition occurs at ~3.5 GPa. The volume compression of the two phases is described by third-order Birch-Murnaghan equations-of-state: \( V_0 = 201.02(1) \, \text{Å}^3 \), \( K_0 = 59.7(5) \, \text{GPa} \), \( K'' = 3.5(3) \) for the low-P polymorph, and \( V_0 = 200.1(13) \, \text{Å}^3 \), \( K_0 = 44(8) \, \text{GPa} \), \( K'' = 6.4(20) \) for the high-P polymorph. The pressure-induced structural evolution in kalsilite up to 7 GPa appears to be completely reversible. The compression of both phases involves tetrahedral rotations around [0001], which close up the channels within the framework. In addition, compression of the low-pressure phase involves tilting of the tetrahedra. The major structural change at the phase transition is an increase in the tilting of the tetrahedra, but with a reversion of the tetrahedral rotations to the value found at ambient conditions. This behavior is in distinct contrast to that of nepheline, which has a tetrahedral framework of the same topology.

Keywords: Crystal structure, kalsilite, XRD data, single crystal, high pressure, compressibility, structural evolution, compressibility measurements

INTRODUCTION

Kalsilite is a feldspatoid with ideal chemical formula: KAlSiO₄. In nature, kalsilite occurs mainly in K-rich and silica undersaturated volcanic rocks, usually associated with olivine, melilite, clinopyroxene, phlogopite, nepheline, and leucite. A few occurrences of metamorphic kalsilites have also been reported (e.g., Sandiford and Santosh 1991). Experiments on the stability of potassium aluminosilicates indicate that kalsilite is stable at least up to 15 GPa at 1300 K and, together with KAl₂Si₂O₈ (hollandite-type) and K₂Si₃O₈ (wadestotype) phases, can be considered a potential host for K in anhydrous hyper-alkaline systems (Liu 1987).

In ceramic technology, kalsilite is used as the precursor for leucite, an important component in porcelain-fused-to-metal and ceramic restoration systems (Zhang et al. 2007). Kalsilite has also been proposed as a high thermal expansion ceramic for bonding to metals (Bogdanovic et al. 2008) and for the production of glass-ceramic seals for use in solid oxide fuel cells (Badding et al. 2009). Recently, nano-sized kalsilite has been demonstrated to show an excellent and highly improved oxidation activity of carbon toward diesel soot combustion (Kimura et al. 2008). Kalsilite is also used as a heterogeneous catalyst for transesterification (a process in which the organic group of an alcohol) of soybean oil with methanol to biodiesel (Wen et al. 2010).

The tetrahedral open-framework of kalsilite is isotypic with that of tridymite and nepheline, and has topological symmetry P6₃/mmc. The kalsilite framework consists of (0001) sheets of (ordered) AlO₄ and SiO₄ tetrahedra forming six-membered rings (hereafter 6mR), pointing alternately up (U) and down (D) [i.e., 6mR//(0001)]. The sheets are stacked along the c-axis and are connected through the apical O1 atoms, which formally lie on special positions on the threefold axes. In volcanic Na-bearing kalsilites, this bridging oxygen may be displaced from the threefold axis (by up to ~0.25 Å), giving Al-O-Si bond angles <180° (Perrotta and Smith 1965). The tetrahedral 6mRs are also di-trigonally distorted by rotation of the tetrahedra around [0001], with the sense of rotation reversed between adjacent (0001) sheets in the P31c polymorph but with the same sense of rotation in all sheets of the P31c polymorph that we have studied. A further set of 6mRs occurs perpendicular to (0001) [Fig. 1, hereafter 6mRL//(0001)] that do not form channels.

Many experiments have been devoted to the phase stability, thermal behavior, and structural evolution at high- and low-temperature of kalsilite, which appear to be strongly controlled by the Na content (Tuttle and Smith 1958; Sahama 1962a, 1962b; Dollase and Freeborn 1977; Gregorkiewicz and Schäfer 1980; Andou and Kawahara 1982, 1984; Henderson and Taylor...
were annealed at 900 °C for 1 h by Cellai and Carpenter (1999),
and had previously exhibited $P6_3$ symmetry at room temperature,
were selected. Surprisingly, all of the crystals checked by single-
   crystall X-ray diffraction showed $P31c$ symmetry: the $P31c$-to-$P6_3$
   phase transition upon heating reported as irreversible by Cellai
   et al. (1997) is actually reversible, on the timescale of a decade.
Gatta et al. (2010a) described the thermo-elastic behavior at low
   $T$ and suggested that the negative thermal expansion along [0001]
   observed between 100 and 300 K is a consequence of a decrease
in the tetrahedral tilts with increasing temperature.

Despite the petrological importance of this mineral and tech-
nological uses of its synthetic counterpart, only one high-pressure
experiment on this open-framework silicate has so far been reported.
Fasshauer et al. (1998) measured the $P$-$V$ equation of state of a syn-
thetic $P6_3$ kalsilite up to 6.1 GPa by X-ray powder diffraction with a
"quasi-hydrostatic" experiment conducted with a solid pressure
medium. The elastic anisotropy is therefore unknown and the crystal-
lographic characterization of the material at ambient conditions
was performed only by the refinement of the unit-cell parameters on the
basis of the powder diffraction pattern. On this basis, the aim of this
study was the investigation of the phase stability, elastic behavior,
and the pressure-induced structural evolution of a (Na-free) $P31c$
   kalsilite by means of in situ single-crystal X-ray diffraction with a
   diamond-anvil cell under hydrostatic conditions.

**EXPERIMENTAL METHODS**

The experiments in this study have been performed using a metamorphic
kalsilite from the sample studied by Carpenter and Cellai (1996) and Cellai et al.
(1997, 1999). The kalsilite crystals were collected from a granulite facies gneiss
from Punalur, Kerala district, southern India, and provided by M. Santosh. In
these rocks, kalsilite coexists with leucite, K-feldspar, hibonite, spinel, corundum,
titanite, perovskite, and Ti-bearing phlogopite. Sandiford and Santosh (1991)
estimated peak metamorphic conditions of the Punalur gneiss as 700–800 °C and
3.5–6.5 kbars. Kalsilite from Punalur is essentially end-member KAISiO$_4$, with a
K/Na molar ratio of ~350 (Capobianco and Carpenter 1989; Sandiford and Santosh

A single crystal (130 × 110 × 40 µm$^3$) of kalsilite was selected for the diffraction
experiments. Precise and accurate unit-cell parameters were first measured with
the crystal in air (Table 1) with a Huber four-circle diffractometer (non-
monochromatized MoK$_\alpha$ radiation) using the eight-position centering protocol (King
and Finger 1979; Angel et al. 2000; Angel and Finger 2011) of 28 Bragg reflections
(Table 1). The lattice was found to be metrically trigonal, with unit-cell parameters
of $a = 5.1606(2)$ Å, $c = 8.7164(1)$ Å, and $V = 201.02(2)$ Å$^3$. Intensity data were
then collected on an Xcalibur-1 Oxford Diffraction diffractometer equipped with a
CCD (Kappa-geometry, graphite-monochromatized MoK$_\alpha$ radiation) with the
parameters reported in Table 2. No evidence of non-Bragg reflections was found.

The crystal of kalsilite was found to be twinned by reticular merohedry with the
{0001} twin plane, as previously observed for the Punalur kalsilite (Cellai et al.
1997; Gatta et al. 2010a). The refined volumes of the two twin components
approached 50% each. The refinement conditions were consistent with space group
$P31c$, in agreement with Cellai et al. (1997, 1999) and Gatta et al. (2010a).
Intensity data were then corrected for Lorentz-polarization (Lp) and absorption effects
(analytical absorption correction by Gaussian integration based upon a physical
description of the crystal) with the CrysAlis software (Oxford Diffraction 2009).
The anisotropic structure refinement was performed with the SHELX-97 software
(Sheldrick 2008), starting from the atomic coordinates of Gatta et al. (2010a), using
neutral atomic scattering factors of K, Al, Si, and O from the International Tables
for Crystallography (Wilson and Prince 1999). The refinement showed no threefold
degeneracy of the oxygen O1 (Table 3). The tetrahedral bond distances indicated

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American Mineralogist Contents, find the table of contents for the specific vol-
ume/issue wanted, and then click on the deposit link there.
With the crystal in the DAC without any pressure, $1/\sigma^2$ was fixed. Estimated standard deviations are in parentheses.

Residuals ($wR$)

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<th>$P$ (GPa)</th>
<th>0.0001</th>
<th>0.0001*</th>
<th>0.90(5)</th>
<th>1.33(10)</th>
<th>2.30(10)</th>
<th>3.05(10)</th>
<th>3.27(10)</th>
<th>4.62(11)</th>
<th>4.94(10)</th>
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<tr>
<td>$a$ (Å)</td>
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<td>5.099(3)</td>
<td>5.081(3)</td>
<td>5.079(4)</td>
<td>5.061(5)</td>
<td>5.048(3)</td>
<td>5.024(2)</td>
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<tr>
<td>$c$ (Å)</td>
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<td>8.637(6)</td>
<td>8.605(4)</td>
<td>8.587(5)</td>
<td>8.315(9)</td>
<td>8.322(6)</td>
<td>8.261(3)</td>
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<td>197.42(6)</td>
<td>194.5(5)</td>
<td>192.4(2)</td>
<td>191.8(2)</td>
<td>184.4(3)</td>
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<tr>
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<td>1340</td>
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<tr>
<td>No. unique reflections</td>
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<td>553</td>
<td>532</td>
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<td>508</td>
<td>448</td>
<td>461</td>
<td>457</td>
<td>426</td>
</tr>
<tr>
<td>No. unique reflections with $F_o &gt; 4\sigma(F_o)$</td>
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<td>244</td>
<td>227</td>
<td>216</td>
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<td>215</td>
<td>184</td>
<td>178</td>
<td>171</td>
<td>158</td>
</tr>
</tbody>
</table>

**Note:** Lattice parameters with the crystal in air are: $a = 5.1660(2)$, $c = 8.7164(1)$ Å and $V = 201.02(2)$ Å$^3$. Estimated standard deviations in the last digit are in parentheses.

* Crystal in the DAC without P-medium.
† In decomposition.

### Table 2. Details of data collection and refinements of kalsilite at different pressures

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**Notes:** For all of the data collections: MoKα radiation, CCD detector type, $\omega$ scan type, 60 s of exposure time per frame. The crystal of kalsilite was twinned by recticular merohedry with the (0001) twin plane, and the refined volumes of the two twin components approached 50% each at all pressures. The Flack parameter ($\xi$) was fixed. Estimated standard deviations are in parentheses.

$R_{\text{int}} = \sum |F_o| - |F_c| / \sum |F_o|$, $R_{\text{merge}} = \sum |F_o| - |F_c| / \sum |F_o|$, $wR = \sum (w(|F_o| - |F_c|)^2) / \sum (w|F_o|)^2$, $w = 1/\sigma^2(|F_o|) + (0.01)^2|F_o|$, $P = \text{Max}(\sum(\sum|F_o|/2))$.

* With the crystal in the DAC without P-medium.
† Refinements with the O1 split-site model.

### Results

#### Unit-cell parameters and elasticity

The evolution of the unit-cell parameters of kalsilite up to about 6.9 GPa is shown in Figure 2. It is clear from these data, and especially from the evolution of the $c/a$ ratio with $P$ (Fig. 2), that there are three distinct regimes in the compressional behavior of kalsilite as well as a first-order phase transition. Between 0.0001 and ~2.5 GPa, a “normal” compressional behavior is observed, with a positive monotonic trend of the $c/a$ ratio with pressure. Above 2.0 GPa, there is a stiffening of the $a$-axis, and between ~2.5 and ~3.5 GPa a pronounced softening of the $c$-axis leading to a decrease in the $c/a$ ratio with $P$. In this last pressure range, all of the Bragg reflections except the 001 reflections show significant broadening, and this resulted in a significant increase of the e.s.d. values of the unit-cell parameters.
This regime appears to be the precursor to a first-order phase transition just above 3.5 GPa that has never been previously reported in the literature. The transition pressure was bracketed between 3.529(8) and 3.600(6) GPa by several reversal measurements in compression and decompression, and we were unable to demonstrate a hysteresis. The phase transition on increasing pressure gives rise to an expansion of the structure on [0001] and to a strong compression along [0001] (Fig. 2) that combine to produce a ~0.4% volume decrease. Optical and diffraction observations show that the phase transition does not lead to a further twinning of the crystal. Above the transition, the Bragg diffraction peaks become sharp again, with the same widths as for the high-pressure phase. The Bragg peaks at 20°-2θ are defined according to Klyne and Prelog (1960). With the crystal in the DAC without any P-medium.

The variation of the volume of the low-pressure polymorph at the pressure of the phase transition, and also of the bulk moduli are compared at room pressure: $V_0 = 200.1(13) \, \AA^3$, $K'_0 = 448(4) \, \text{GPa}$, $K''_0 = 6.4(20)$.

The $fe$-$Fe$ plots (Fig. 3) show that the variation of both unit-cell parameters of the high-pressure polymorph can be described in terms of a second-order linearized BM EoS (Angel 2000) with $K' = 4$. Weighted fits give: $a_0 = 5.170(1) \, \AA$ and $K_{\text{EoS}}(a) = 59.8(6) \, \text{GPa}$ for the $a$-axis and $c_0 = 8.575(1) \, \AA$ and $K_{\text{EoS}}(c) = 47.8(3) \, \text{GPa}$ for the $c$-axis, showing that the [0001] axis is about 25% stiffer in compression than the perpendicular [0001] axis. The behavior of the unit-cell parameters of the low-pressure polymorph is much more complex (Fig. 3), and neither can be described by a single equation of state. We therefore fit the data only up to pressures at which significant abnormal compression occurs, purely to obtain a reasonable estimate of the low-pressure compressional moduli. The refined elastic parameters for the low-Pressure polymorph are: $a_0 = 5.1602(1) \, \AA$ and $K_{\text{T0}}(a) = 52.0(3) \, \text{GPa}$ with $K'_{\text{fixed}} = 4$ for the $a$-axis data up to 1.6 GPa, and $c_0 = 8.7166(2) \, \AA$ and $K_{\text{T0}}(c) = 89.7(7) \, \text{GPa}$ and $K''_{\text{fixed}} = -6.2(4) \, \text{GPa}$ for the $c$-axis up to 2.62 GPa. The elastic anisotropy of the low-pressure phase with the [0001] axis being stiffer than the [0001] plane is the reverse of that in the high-pressure phase. Note the strongly negative value for $K''$ of the $c$-axis that indicates that elastic softening occurs prior to the phase transition.
Structural evolution with pressure: tetrahedral framework

Within the average structure of P31c kalsilite at room conditions, the tetrahedral T1 and T2 sites and the bridging O1 oxygen lie on the triad axis (at x = 1/3, y = 2/3), which makes the T1-O1-T2 linkage linear. Therefore, if the kalsilite structure conforms strictly to the global P31c symmetry, the only degrees of freedom available to accommodate compression are tetrahedral compression and deformation of the O-T-O bond angles, and the rotation of the tetrahedra around [0001]. To describe the rotations, we define a rotation angle “δ” that describes the rotation of the tetrahedra from the un-rotated state they would have in the (hypothetical) structure with the topochanical symmetry P6/mc (Gottardi 1979; Fig. 4a). Because all of the O2 atoms in one layer of tetrahedra have the same z-coordinate by symmetry in both P31c and P6/mc, the O2-O2-O2 angles can be used to define the tetrahedral rotation as δ = |120 − (O2-O2-O2)/2 (Fig. 4b). When the tetrahedra are not rotated, the O2-O2-O2 angles are all 120°. Rotation reduces and increases adjacent O2-O2-O2 angles by the same amount, so that two adjacent angles in the ring always sum to 240°. Using the absolute value in the numerator in the expression for δ ensures that the same value is obtained whichever of the two O2-O2-O2 angles is used. The maximum possible rotation of δ = 30° corresponds to O2-O2-O2 angles of 60° and 180°. In kalsilite at room conditions, the O2-O2-O2 angles are 78.4° and 161.6°, so the rotation angle δ is 20.8°. The projected triangle T1-O2-T2 (Fig. 4b) also provides the relationship between the length of the cell edge, a, and the rotation angle as \( a/\sqrt{3} = 2l \cos \delta \), where l is the average of the lengths of the T1-O2 and T2-O2 bonds projected on to the (0001) plane. Thus, if the tetrahedra are rigid, rotations increase δ and reduce the a unit-cell parameter.

There is strong evidence that in the local structure of kalsilite the tetrahedra are tilted in addition to being rotated. The T1-T2 distance across the O1 oxygen of ~3.32 Å is too short at room conditions to accommodate normal values for Al-O and Si-O bonds. The large values of the thermal displacement parameter \( U_{11} \) for the O1 oxygen suggest static or dynamic displacements from the triad at x = 1/3, y = 2/3. The large value at room conditions of \( U_{11} \) for the O2 basal oxygen of the tetrahedra (Table 3) suggests that the O1 displacement is due to local tilting of the tetrahedra that locally breaks the P31c symmetry (e.g., Gatta et al. 2010a). The tilting in kalsilite is not as large at room conditions as the one observed in nepheline, and it is not possible to refine a split-site model for the O1 position for kalsilite. The O1 site
**Figure 3.** Volume and axial Eulerian finite strain vs. normalized stress (fe-Fe plot) for kalsilite; e.s.d. values calculated according to Heinz and Jeanloz (1984) and Angel (2000), including the measured uncertainty in $V_0$, $a_0$, and $c_0$. The dashed and solid lines represent the weighted linear regressions through the data points for the low-P and high-P polymorphs, respectively, and the refined $Fe(0)$ and $K'$ values are reported. For the high-P polymorph, strain, and stress were calculated using the $a_0$, $c_0$, and $V_0$ values refined with a Birch-Murnaghan EoS fit, and the error bars include the uncertainties in these values.

**Figure 4.** (a) A single $6mR$ of kalsilite viewed down [0001] with zero rotation and space group symmetry $P6_3mc$, equal to the topochemical symmetry. (b) The rotated $6mR$ in $P31c$ kalsilite at room conditions. The rotation angle is defined as the angle between the projections on to (0001) of the T1-T2 vector (solid line) and the T1-O2 and T2-O2 vectors (broken lines), and is: $\delta = |\angle T1 - (O2-O2-O2)|/2$. 

low-P polymorph: $Fe(0) = 59.8(2)$ GPa
$K' = 3.4(2)$

high-P polymorph: $Fe(0) = 44.6(8)$ GPa
$K' = 6.6(4)$
is therefore formally located at (1/3, 2/3, z), but the significantly anisotropic thermal displacement ellipsoid indicates an average over a true local structure with T1-O1-T2 angles less than 180°. If we consider normal Al-O and Si-O bond lengths at room conditions of 1.73 and 1.62 Å, respectively, we can estimate from the T1-T2 distance obtained from the data set collected in the DAC that the local value of the T1-O1-T2 angle is ~165° at 0.0001 GPa, corresponding to a tilt of the tetrahedra of φ = 10.5°, and a T1-O1-T2 angle of ~159° at 2.30 GPa. In contrast, the combined effect of the rotation and tilting of rigid tetrahedra is significantly greater than that required to explain the decrease in the c unit-cell parameter, indicating that some additional structural relaxation, such as changes in the O-T-O angles, occurs within the tetrahedra.

\[ \angle \text{O1-O2-O2} \approx 120° \]

\[ \angle \text{T1-O1-T2} \approx 159° \]

\[ \angle \text{T2-O1-T2} \approx 159° \]

\[ \angle \phi \approx 10.5° \]

\[ \angle \delta \approx 20° \]

\[ \angle \theta \approx 10° \]

\[ \angle \psi \approx 10° \]

\[ \angle \gamma \approx 10° \]

\[ \angle \alpha \approx 10° \]

\[ \angle \beta \approx 10° \]

\[ \angle \gamma' \approx 10° \]

\[ \angle \delta' \approx 20° \]

\[ \angle \phi' \approx 10° \]

\[ \angle \theta' \approx 10° \]

\[ \angle \psi' \approx 10° \]

\[ \angle \gamma' \approx 10° \]

\[ \angle \alpha' \approx 10° \]

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\[ \angle \gamma'' \approx 10° \]

\[ \angle \delta'' \approx 20° \]

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Phase transition

Structure refinements confirm that the high-pressure polymorph maintains the same $P3_1c$ symmetry as the low-pressure polymorph. The crystal of the high-pressure polymorph is twinned by reticular merohedry with the $\{0001\}$ twin plane, as observed for the low-pressure polymorph, and the refined volumes of the two twin components approach 50% each. The displacement parameters of both oxygen positions are significantly larger in the high-pressure phase than below the transition and therefore indicate that the tetrahedral tilts increase through the transition. This increase in tilts is sufficient to allow the stable refinement of a model with the O1 displaced from the threefold axis, to a general $(x,y,z)$ position with site occupancy factor fixed to 1/3 (Table 3), as has previously been refined for volcanic kalsilite (e.g., Perrotta and Smith 1965) and nepheline (e.g., Angel et al. 2008). The quality of the refinements with the O1-split model is superior (Table 1) to those with the O1 located on the triad, and the resulting tilts are 13.5° (Fig. 5) with a T-O-T angle of ~153°. Note that the value of the tilt obtained from these refinements is smaller than that predicted from the T1-T2 distance assuming that the T-O1 distances remain constant, and this provides independent confirmation that not only do the tilts increase but that the T-O bond lengths decrease at the transition.

Thus, the reduction in the $c$ unit-cell parameter at the transition (Fig. 2) is the result of increased tilting. The transition is also accompanied by significant internal deformation of the tetrahedra as measured by the changes in the internal O2-T-O2 bond angles (Table 4), but these do not contribute to the volume reduction. The expansion in the (0001) plane arises from a reduction of the rotation angle of the tetrahedra back to approximately the value found at room pressure, which overcomes the combined effects of the increase in tilt and the compression of the T-O bond lengths.

$\sim3.6 < P < \sim6.2$ GPa

Further compression of the high-pressure phase is significantly different from that in the low-pressure phase in that the tilts of the tetrahedra remain constant, so the compression of the $c$-axis is accommodated by compression of T-O2 bonds and the sliding of the tetrahedra past one another as seen in the pre-transition interval; this is also apparent from the evolution of the torsion angles (Table 4). The bond shortening also contributes to the compression of $a$, which is shortened by the re-initiation of increased rotations of the tetrahedra (Fig. 5a).

Structural evolution with pressure: Extra-framework content

The evolution of the tetrahedral framework of kalsilite with $P$ defines the changes in the configuration of the extra-framework K-polyhedron. Within the stability field of the low-$P$ polymorph (i.e., 0.0001–3.5 GPa), the increase in tetrahedral rotations causes the shorter K-O bond distances to compress faster than the longer ones, so that there is a slight increase in the anisotropy of the K-coordination (Table 4). Because the position of the O1 atom on the triad is an average position, no significance can be attributed to the values of K-O1 distances.

The first-order phase transition at ~3.5 GPa, with the drastic contraction along [0001] and the expansion on (0001), drives the structure toward a different channel configuration. At 4.62 GPa, the K-polyhedron is much more anisotropic, with three significantly shorter K-O2 bonds and three longer ones that differ by ~0.41 Å (Table 4). Further compression of the high-pressure phase leads to a faster compression of the longer K-O2 bonds so the anisotropy appears to become slightly less pronounced. A similar trend, toward a more anisotropic configuration, was observed for K-polyhedra in other classes of silicates at high pressure with the cation similarly coordinated by O atoms of double 6mRs of tetrahedra (Gatta et al. 2009, 2010b).

Discussion and conclusions

This is the first experiment in which the behavior of kalsilite, with $P3_1c$ symmetry, has been investigated at high pressure by means of single-crystal X-ray diffraction. Kalsilite experiences an iso-symmetric first-order phase transition at 3.5–3.6 GPa. The
phase transition is displacive in character and reversible, with no detectable hysteresis through the pressure intervals used in this study. The transition gives rise to a small expansion of the structure in the (0001) plane and a strong contraction along [0001]. The low-\(P\) polymorph is less compressible than the high-\(P\) one, a behavior already observed in other open-framework silicates belonging to the Na\(_2\)O\(_2\)K\(_2\)O-Al\(_2\)O\(_3\)-Si\(_2\)O\(_5\) system (Gatta et al. 2006, 2008). The elastic parameters reported by Fasshauer et al. (1998) for a synthetic \(P_6_3\) kalsilite on the basis of a Murnaghan Eq of state (Murnaghan 1937) to the \(P-V\) data (i.e., \(K_{\text{Nh}} \approx 58.6\) GPa, \(K' = 0.1\) differ significantly from those obtained here, but it is not clear whether this difference represents a true difference between the polymorphs, or the effects of non-hydrostaticity in the experiments by Fasshauer et al. (1998).

Angel et al. (2008) and Gatta et al. (2010a) described the low-temperature structural evolution and thermo-elastic behavior of nepheline and kalsilite, respectively, showing that these two isotypic compounds do not respond to changes in temperature in the same way. Nepheline, in fact, has four independent tetrahedral sites (i.e., T1, T2, T3, and T4) that form a framework with two distinct \(6m\)\(R_3\)//(0001) in two different configurations (to produce large cavities for K and smaller cavities in which the smaller Na cations occupy \(1/4\) of the channel sites). The more expanded of the two rings in nepheline, which has trigonal symmetry, is far less distorted than the rings in kalsilite. At room conditions, the diffraction pattern of \(P_6\) nepheline includes satellite reflections, and the structure refinement to the Bragg reflections shows that the O1 site is displaced from the triad at 2/3, 1/3, \(z\) (Gatta and Angel 2007; Angel et al. 2008). In their comparative analysis of the low-\(T\) behavior of kalsilite and nepheline, Gatta et al. (2010a) highlighted how the nature of the extra-framework population, through its bonding to the framework O atoms, can play a fundamental role in determining the structural response to temperature changes. The main deformation mechanism observed in kalsilite at low \(T\) reflects the mechanism observed here at high pressure for both the \(P\)-polymorphs: a cooperative anti-rotation of all tetrahedra of the \(6m\)\(R_3\)//(0001) around [0001], as shown in Figure 5a.

At high pressure, Gatta and Angel (2007) observed a change in the compression mechanisms of nepheline arising from the changes in the O1 position associated with changes in the compression of the unit-cell axes and the unit-cell volume. The authors observed that, at 1.8 GPa, no significant intensity of the satellites occurred, the O1 site moved toward the triad, and thus the tilts of the T1 and T2 tetrahedra decreased. The presence of the subsidiary non-Bragg reflections was therefore related to the split of the O1 site. When the satellites disappear at pressures above 2 GPa, the O1 site is located on the triad (at 2/3, 1/3, \(z\)), leading to a straight T1-O1-T2 bond and thus the tilts of the T1 and T2 tetrahedra decreased to zero. Therefore, two main deformation mechanisms occur in nepheline: below 2 GPa, the structure responds to increased pressure by decreasing tilting of the T1 and T2 tetrahedra and increased tilting of the T3 and T4 tetrahedra, but above 2 GPa by tilting of the T3 and T4 tetrahedra alone. The change in the compressional mechanisms of nepheline does not lead to any phase transition. The elastic behavior was modeled by a fourth-order BM-EoS, with parameters: \(V_0 = 723.57(4)\) \(\text{Å}^3\), \(K_0 = 47.32(26)\) GPa, \(K' = 2.77(24)\) and \(K'' = 0.758(79)\) GPa\(^{-1}\), showing that nepheline is more compressible than the low-\(P\) kalsilite. The symmetry of (Si/Al “ordered”) nepheline, the presence of four independent tetrahedral sites (i.e., T1, T2, T3, and T4) and, in particular, the nature of the extra-framework population (i.e., K, Na, Ca, and 20–25% site vacancies, Gatta and Angel 2007; Angel et al. 2008) govern the higher degree of freedom of nepheline in response to \(T\) and \(P\).

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References Cited


