Compressibility of a natural kyanite to 17.5 GPa

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Abstract

The compressional behaviour of a natural kyanite, (Al\textsubscript{1.99}Fe\textsubscript{0.01})SiO\textsubscript{5}, has been investigated to about 17.5 GPa at 300 K using a diamond-anvil cell and synchrotron X-ray diffraction. The pressure-volume data fitted to the third-order Birch–Murnaghan equation of state (EoS) yield an isothermal bulk modulus ($K_0$) of 192 ± 6 GPa and pressure derivative ($K_0''$) of 6 ± 1. When $K_0''$ is fixed as 4, the derived $K_0$ is 201 ± 2 GPa. These values are in excellent agreement with most experimental determinations in the literature. Consequently, it can be concluded that the compressibility of kyanite under high pressures has been accurately constrained.

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Keywords: Compressibility; High-pressure; Isothermal bulk modulus; Kyanite; Synchrotron X-ray diffraction

1. Introduction

Kyanite, the high-pressure polymorph of Al\textsubscript{2}SiO\textsubscript{5} [1], is an important constituent phase for the materials of continental crust and pelagic sediment at pressures from ~1 to ~16 GPa [2,3]. It plays a significant role in a large number of geological reactions, which may involve phases like paragonite, zoisite, lawsonite, pumpellylite, chloritoid, staurolite, and stishovite [4–8]. In order to fully understand these reactions and their phase relations, apparently, it is necessary to accurately constrain the thermodynamic properties of kyanite, one of which is the elasticity.

The elastic properties of kyanite have not been well determined so far, although quite a few studies with different methods including high pressure experimentation and theoretical calculation have been carried out [9–16]. Brace et al. [9] conducted a pioneering but preliminary experimental investigation on a synthetic mixture of kyanite powder and powder of lead or copper and determined a bulk modulus ($K_0$) of 130 ± 10 GPa for kyanite. With an experimental study of the decomposition of kyanite to stishovite and corundum, Irifune et al. [10] thermodynamically arrived at the conclusion that the bulk modulus of kyanite is probably around 202 ± 15 GPa ($K_0''$ of all involved phases fixed as 4). Both Comodi et al. [12] and Yang et al. [13] conducted a single-crystal X-ray diffraction study on kyanite, and they constrained the bulk modulus of kyanite to be 160 ± 3 and 193 ± 1 GPa ($K_0''$ fixed as 4), respectively. The most recent experimental investigation on the elasticity of kyanite was done by Friedrich et al. [16], who obtained the bulk modulus of kyanite to be 190 ± 3 ($K_0''$ fixed as 4). On the other hand, theoretical calculations conducted to investigate the compressibility of kyanite also show some discrepancies [11,14,15]. Molecular dynamics simulation determined a value of 197 GPa for the isothermal bulk modulus of kyanite [11], whereas \textit{ab initio} simulation suggested a value of 172 GPa ($K_0''$ fixed as 4.1) [14]. Using density functional theory with a generalized

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our natural kyanite is approximately (Al 1.99Fe0.01)SiO5.

and 0.31% Fe 2O3 (by weight), with all other components
kyanite has a composition of 36.62% SiO2, 62.72% Al 2O3
hosted at the Department of Earth Sciences, University
uct was analysed by an X-ray fluorescence spectrometer
under acetone in an agate mortar. Part of the powder prod-
source were carefully crushed and thoroughly ground
2. Experimental details

Bluish crystals of a natural kyanite with an unknown
source were carefully crushed and thoroughly ground
under acetone in an agate mortar. Part of the powder product was
analysed by an X-ray fluorescence spectrometer hosted at the
Department of Earth Sciences, University of Western Ontario; the analysis showed
that this natural kyanite has a composition of 36.62% SiO3, 62.72% Al2O3
and 0.31% Fe2O3 (by weight), with all other components
negligible. No specific method was used to check the charge
density of iron; according to Burns [17], rather, we assumed

Consequently, the chemical formula of
our natural kyanite is approximately (Al1.99Fe0.01)SiO5.

Part of the powder product was checked by a powder X-ray
diffraction hostometer at the School of Earth and Space
Sciences, Peking University (X’Pert Pro MPD system; Cu
Kα1 X-ray radiation). Kyanite was confirmed to be the
only solid crystalline phase, with the unit-cell parameters

\[ a = 7.115(2) \text{ Å}, \quad b = 7.841(2) \text{ Å}, \quad c = 5.573(2) \text{ Å}, \quad \alpha = 90.01(3) ^\circ, \quad \beta = 101.13 ^\circ(3) \quad \gamma = 105.96 ^\circ(3) \]

which are essentially identical to those values given by the JCPDS reference
pattern card 11-46. Its ambient pressure unit-cell volume was
determined to be 292.8 ± 0.1 Å³, slightly smaller
than that of the kyanite from Minas Gerais, Brazil
(293.9 ± 0.3 Å³ in [12]; 293.31 ± 0.02 Å³ in [13]). This
minor volume difference might be caused by the difference in
the compositions of these two kinds of kyanite; the
chemical formula of the kyanite from Minas Gerais, Brazil,
is Al1.98Fe0.02SiO5 (iron was assumed to present as Fe3+)
[12].

We conducted our high-pressure angle dispersive X-ray
diffraction experiments up to about 17.5 GPa with a sym-
etrical diamond-anvil cell at the beamline X17C,
National Synchrotron Light Source, Brookhaven National
Laboratory, USA. In general, the experimental techniques
used here were very similar to those reported by Liu et al.
[18]. T301 stainless steel plates with an initial thickness of
250 µm were used as gaskets. The central area of the plates
was pre-indent to a thickness of about 30 µm, and a hole
of 150 µm in diameter was subsequently eroded electrically.
The kyanite powder, along with a couple of tiny ruby balls,
was loaded with the pressure medium (a 4:1 methanol-eth-
anol mixture which should solidify at about 10 GPa at
300 K) into the hole in the gasket. With the ruby fluores-
cence method [19], the experimental pressure was measured
before and after each X-ray analysis. The incident synchro-
tron radiation beam was monochromatized to a wave-
length of 0.4066 Å, and its beam size was collimated to a
diameter of ~25 × 20 µm². The X-ray diffraction pattern
of the sample at certain pressure was collected with an
exposure time of 10 min using an online CCD detector,
and later integrated as a function of 2θ to give the
conventional one-dimension X-ray profile using the Fit2D
program [20].

Kyanite has the lowest symmetry (P1) and large unit-
cell parameters [12,13]. Consequently, it has to be
probed, as required by the Bragg Law, by X-ray radia-
tion with long wavelength, in order to achieve good res-
olution. As shown in Fig. 1, even with the Cu Kα1 X-ray radiation, some peak overlapping is still inevitable; for
instance, peak 2 211 slightly overlaps with peak
2 2 11, peak 1 1 3 0 with peak 1 1 3 0, peak 0 1 2 with
peak 0 3 0, peak 0 2 1 2 with peak 0 2 3 0, peak 1 1 2 with
peak 2 1 2, peak 1 3 1 with peak 3 3 1. Only with
great care could these overlapping peaks be successfully
separated by the Peakfit program. The shorter wave-
length of the synchrotron X-ray radiation exacerbates
the problem, and more intense peak overlapping has been
observed (Fig. 1). Lucky enough, however, there are still
many free-standing peaks as shown in Fig. 1, and
not all of the overlapping peaks are completely unresolved by the Peakfit program. Therefore, the
unit-cell parameters of kyanite, calculated by refining
the unit cell using the positions of the strongest and most
unambiguous diffraction peaks, such as 1 1 1, 0 2 0,
0 2 0, 2 1 1, 0 2 1, −2 2 0, 0 4 0, −4 1 1, and 1 1 3,
can be constrained with high confidence. The good agreement
in the unit-cell parameters of kyanite constrained by the
conventional powder X-ray radiation and by the synchro-
tron is an indicator of the success of the experimental
method used in this study.

![Fig. 1. Ambient synchrotron powder X-ray diffraction (wavelength = 0.4066 Å) versus conventional powder X-ray diffraction (Cu Kα1; a wavelength of 1.5405 Å was used in collecting the data which, when plotted here, have been recalculated to the wavelength of 0.4066 Å, for the purpose of comparison). Apparently, the synchrotron analysis has a lower resolution, due to the shorter wavelength of the synchrotron X-ray radiation and the low symmetry (P1) of kyanite. In order to show the data clearly, overlapping but probably resolvable major peaks and minor peaks from the kyanite sample are not indexed for the synchrotron powder X-ray diffraction pattern.](image-url)
3. Result and discussion

Experiments were carried out up to 17.5 GPa at room temperature. No phase transition, transformation or amor-phization was found over this pressure range (Fig. 2), which in general confirmed the observation made by Fried-rich et al. [16]. According to the experimental and theoret-ical investigations in the literature [7,8,10,14,21–23], kyanite, at room temperature, can be stable at pressures up to only about 12 GPa. Apparently, the data we collected at pressures higher than 12 GPa were from the metastable field of kyanite.

The effect of pressure on the unit-cell parameters is sum-marized in Table 1 and graphically shown in Figs. 3 and 4. The pressure dependence of the unit-cell parameter \(a\) by \(b = 7.838(\pm 4) - 0.0137(\pm 11)P + 0.00023(\pm 6)P^2\), and that of the unit-cell parameter \(c\) by \(c = 5.572(\pm 3) - 0.0114(\pm 7)P + 0.00023(\pm 4)P^2\), with \(a\), \(b\), \(c\) in Å and \(P\) in GPa (Fig. 3). This observation is not completely consistent with the observations made by Yang et al. [13] and Comodi et al. [12], in which unit-cell parameters \(a\), \(b\), \(c\) of kyanite varied linearly with pressure; Yang et al. [13] and Comodi et al. [12] limited the pressure of their experi-ments up to 4.56 and 5.80 GPa, respectively, so that the effect of pressure on these unit-cell parameters might have not fully shown up. The variation of the unit-cell parameters \(x\), \(\beta\) and \(\gamma\) of kyanite with pressure is shown in Fig. 4: \(x\) seems to increase while \(\beta\) and \(\gamma\) seem to decrease slightly with pressure increase. This observation is generally in agreement with Yang et al. [13], although our synchrotron data on a powdered sample are not as accurate as the

Table 1
Unit-cell parameters of kyanite at different pressures.

<table>
<thead>
<tr>
<th>(P) (GPa)</th>
<th>(a) (Å)</th>
<th>(b) (Å)</th>
<th>(c) (Å)</th>
<th>(x) (°)</th>
<th>(\beta) (°)</th>
<th>(\gamma) (°)</th>
<th>(V) (Å³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0001</td>
<td>7.114(1)</td>
<td>7.835(2)</td>
<td>5.568(1)</td>
<td>89.94(2)</td>
<td>101.20(2)</td>
<td>105.91(2)</td>
<td>292.33(9)</td>
</tr>
<tr>
<td>0.88(0)</td>
<td>7.104(3)</td>
<td>7.828(4)</td>
<td>5.560(3)</td>
<td>89.92(7)</td>
<td>101.22(8)</td>
<td>106.16(9)</td>
<td>290.84(19)</td>
</tr>
<tr>
<td>2.21(3)</td>
<td>7.097(1)</td>
<td>7.814(2)</td>
<td>5.548(1)</td>
<td>89.88(4)</td>
<td>101.10(3)</td>
<td>106.41(4)</td>
<td>289.15(9)</td>
</tr>
<tr>
<td>3.87(8)</td>
<td>7.071(1)</td>
<td>7.777(3)</td>
<td>5.536(1)</td>
<td>89.87(3)</td>
<td>101.26(1)</td>
<td>106.12(2)</td>
<td>286.4(1)</td>
</tr>
<tr>
<td>4.58(6)</td>
<td>7.072(4)</td>
<td>7.784(3)</td>
<td>5.528(3)</td>
<td>90.03(7)</td>
<td>101.13(5)</td>
<td>106.24(6)</td>
<td>286.2(2)</td>
</tr>
<tr>
<td>5.8(2)</td>
<td>7.060(3)</td>
<td>7.768(2)</td>
<td>5.517(2)</td>
<td>90.01(5)</td>
<td>101.09(4)</td>
<td>106.36(5)</td>
<td>284.1(1)</td>
</tr>
<tr>
<td>6.70(8)</td>
<td>7.052(2)</td>
<td>7.756(2)</td>
<td>5.506(1)</td>
<td>89.97(4)</td>
<td>101.10(3)</td>
<td>106.36(4)</td>
<td>283.1(1)</td>
</tr>
<tr>
<td>7.9(2)</td>
<td>7.028(2)</td>
<td>7.746(2)</td>
<td>5.500(1)</td>
<td>90.01(4)</td>
<td>101.14(3)</td>
<td>106.33(4)</td>
<td>281.5(1)</td>
</tr>
<tr>
<td>8.8(1)</td>
<td>7.032(5)</td>
<td>7.732(5)</td>
<td>5.493(3)</td>
<td>90.02(9)</td>
<td>101.03(7)</td>
<td>106.41(9)</td>
<td>280.7(2)</td>
</tr>
<tr>
<td>9.6(1)</td>
<td>7.020(2)</td>
<td>7.725(1)</td>
<td>5.481(1)</td>
<td>90.03(3)</td>
<td>101.10(3)</td>
<td>106.33(3)</td>
<td>279.41(6)</td>
</tr>
<tr>
<td>10.7(2)</td>
<td>7.030(4)</td>
<td>7.714(3)</td>
<td>5.471(2)</td>
<td>90.14(7)</td>
<td>100.99(6)</td>
<td>106.26(7)</td>
<td>278.0(2)</td>
</tr>
<tr>
<td>11.6(2)</td>
<td>7.000(2)</td>
<td>7.716(1)</td>
<td>5.468(1)</td>
<td>90.20(4)</td>
<td>101.03(4)</td>
<td>106.22(4)</td>
<td>277.85(8)</td>
</tr>
<tr>
<td>12.8(2)</td>
<td>6.986(2)</td>
<td>7.705(2)</td>
<td>5.459(1)</td>
<td>90.22(4)</td>
<td>100.95(4)</td>
<td>106.20(4)</td>
<td>276.48(9)</td>
</tr>
<tr>
<td>15.5(3)</td>
<td>6.944(3)</td>
<td>7.667(4)</td>
<td>5.458(3)</td>
<td>89.85(1)</td>
<td>101.38(7)</td>
<td>106.11(7)</td>
<td>273.2(2)</td>
</tr>
<tr>
<td>17.5(1)</td>
<td>6.910(3)</td>
<td>7.673(3)</td>
<td>5.449(2)</td>
<td>90.13(6)</td>
<td>100.84(4)</td>
<td>106.34(4)</td>
<td>271.4(1)</td>
</tr>
</tbody>
</table>

Note: X-ray data at ambient pressure were collected on a kyanite powder sample loosely packed into a small hole (400 μm across) in a stainless steel plate; the numbers in parentheses represent one standard deviation in the right-most digit.
single-crystal X-ray data of Yang et al. [13]. One interesting phenomenon shown by our data in Fig. 4 is that the unit-cell parameter $c$ seems to have a large jump when pressure is first applied to the sample (data at 0.0001 versus data at 0.88 GPa).

The $P$–$V$ data of kyanite from this study are compared in Fig. 5 with the $P$–$V$ data collected by Yang et al. [13] and Comodi et al. [12]. Although the zero-pressure volumes are slightly different, the compressibility of kyanite established in our study is much comparable to that determined by Yang et al. [13], since the trends shown by these two sets of data are almost parallel. The data from Comodi et al. [12], however, show a much more compressible property for kyanite.

In order to determine the elastic parameters, the $P$–$V$ data from our study have been fitted to the third-order Birch–Murnaghan equation of state [24] by a least-squares method:

$$P = 3K_{0T}f_E(1 + 2f_E)^{3/2}$$

where $P$ is the pressure (GPa), $K_{0T}$ the isothermal bulk modulus (GPa), $K'_{0T}$ the first pressure derivative of $K_{0T}$, and $f_E$ the Eulerian definition of finite strain, which is $[(V_0/V)^{2/3} - 1]/2$. In the Eulerian definition of finite strain, $V_0$ is the volume at zero pressure, whereas $V$ is the volume at high pressure. When $K'_{0T}$ is set as 4, the isothermal bulk modulus ($K_{0T}$) of kyanite is determined as 201 ± 2 GPa, whereas the zero-pressure volume is determined as 292.2 ± 0.1 Å$^3$. If $K'_{0T}$ is not fixed, the results of our best data-fitting are $K_{0T} = 192 ± 6$ GPa, $K'_{0T} = 6 ± 1$, and $V_0 = 292.3 ± 0.1$ Å$^3$.

The EoS data of kyanite can be evaluated by the plot of the normalized pressure ($F$, GPa) and the Eulerian strain ($f_E$), where $F$ is defined as

$$F = \frac{P}{3f_E(1 + 2f_E)^{5/2}}$$

Fig. 6 shows that the datum points define an almost horizontal line, suggesting that a second-order equation of state or a third-order equation of state with $K'_{0T}$ fixed as 4 can adequately describe the $P$–$V$ data. We consequently conclude that the bulk modulus and its pressure derivative of kyanite determined in this investigation are about 201 GPa and 4, respectively.

The equations of state of kyanite constrained by the studies in the literature and this study are summarized in Table 2. With the exception of Comodi et al. [12], all other experimental investigations gave out similar values for the isothermal bulk modulus of kyanite (from 190 to 202 GPa with $K'_{0T}$ fixed as 4), whatever the experimental methods (phase equilibrium study versus direct compression; Irifune et al. [10] versus Yang et al. [13], Friedrich et al. [16] and this study) and the experimental details (conventional single-crystal X-ray diffraction versus in situ powder diffraction).
The numbers in parentheses represent one standard deviation.

Table 2
Bulk modulus and first pressure derivative of kyanite.

<table>
<thead>
<tr>
<th>Data source</th>
<th>$K_0T$ (GPa)</th>
<th>$K'_0T$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Experimental study</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Irifune et al. [10]</td>
<td>202(15)</td>
<td>4</td>
</tr>
<tr>
<td>Comodi et al. [12]</td>
<td>160(3)</td>
<td>4</td>
</tr>
<tr>
<td>Comodi et al. [12]</td>
<td>156(10)</td>
<td>5.6(5.5)</td>
</tr>
<tr>
<td>Yang et al. [13]</td>
<td>193(1)</td>
<td>4</td>
</tr>
<tr>
<td>Friedrich et al. [16]</td>
<td>190(3)</td>
<td>4</td>
</tr>
<tr>
<td>This study</td>
<td>201(2)</td>
<td>4</td>
</tr>
<tr>
<td>This study</td>
<td>192(6)</td>
<td>5.7(1.1)</td>
</tr>
<tr>
<td><strong>Theoretical study</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Oganov and Brodholt [14]</td>
<td>172</td>
<td>4.1</td>
</tr>
<tr>
<td>Winkler et al. [15]</td>
<td>178</td>
<td></td>
</tr>
</tbody>
</table>

synchrotron X-ray diffraction; Yang et al. [13] versus Friedrich et al. [16] and this study) were. Comodi et al. [12] obtained a 20% smaller bulk modulus (160 GPa with $K'_0T$ fixed as 4), which might have resulted from their poor choice of single crystals that were experimentally investigated. As they noticed, because of the perfect (1 0 0) cleavage of kyanite, all their selected crystals had [1 0 0] which coincided with the diamond-anvil cell axis, and therefore access to the reciprocal lattice was reduced in that direction. With all the experimental data under consideration, we summarily suggest that the bulk modulus and its pressure derivative of kyanite determined by the experimental studies are about 196 ± 6 GPa and 4, respectively. On the line of theoretical calculation, Matsui [11] gave out a value of 197 GPa, which perfectly matched with the experimental determination. Oganov and Brodholt [14] and Winkler et al. [15] suggested slightly smaller values of 172 and 178 GPa, respectively; this underestimation, however, might be due to the underbinding in the density functional theory with a generalized gradient approximation approach. Additionally, the values given by Oganov and Brodholt [14] and Winkler et al. [15] were for 0 K, instead of for room temperature.

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