

Effects of pressure on the structure of bikitaite

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Abstract: The structural behaviour of bikitaite, $\text{Li}_2(\text{Al}_2\text{Si}_4\text{O}_{12}) \cdot 2\text{H}_2\text{O}$, was investigated under hydrostatic pressure using X-ray single-crystal diffraction data. A Merrill-Bassett diamond anvil cell was mounted with glycerol, as non penetrating pressure-transmitting medium, ruby chips and a small crystal of quartz as the calibrant. A strong anisotropic compression was observed by linear regressions of lattice parameters against P , bikitaite being softer along the c axis ($\beta_c = 9.3(1) \cdot 10^{-3} \text{ GPa}^{-1}$), than along b ($\beta_b = 6.6(1) \cdot 10^{-3} \text{ GPa}^{-1}$) and a ($\beta_a = 2.4(1) \cdot 10^{-3} \text{ GPa}^{-1}$) ($\beta_a : \beta_b : \beta_c = 1 : 2.75 : 3.9$). Fitting the cell-volume - pressure data to a second order Birch-Murnaghan equation of state, as indicated by the finite strain-stress plot, yielded $K_0 = 44.2(4) \text{ GPa}$, with $K' = 4$ and $V_0 = 295.58(2) \text{ \AA}^3$.

The evolution of the bikitaite structure with P was studied by comparing the results of refinements with data collected at room conditions, at 3.2 GPa and after decompression. The structure can be described as sheets of six-membered rings parallel to (001), connected by pyroxene-like chains. 8-ring and 5-ring channels run along [010] and inside the 8-ring channel there is a one-dimensional chain of water molecules, which is linked to the framework through the extra-framework Li atoms. Under pressure, the kinking of the pyroxene-like chain decreased the free diameters of the 5-ring channels, strongly reducing the distance between the ab planes. On the contrary, the tridymite-like planes with 6-membered rings were more rigid. The positions of the extra-framework cations and water were maintained at HP even though the configuration of the water chains changed slightly: the distances between the water molecules decreased, whereas the kinking angle of the chain increased.

Key-words: zeolite, bikitaite, single-crystal X-ray diffraction, high-pressure, compressibility.

Introduction

Bikitaite, $\text{Li}_2(\text{Al}_2\text{Si}_4\text{O}_{12}) \cdot 2\text{H}_2\text{O}$, is a rare Li-zeolite with BIK structural type (Meier *et al.*, 1996). According to Gottardi & Galli (1985) the crystal structure of bikitaite shows structural similarities to mordenite. It is the only natural zeolite with mono-dimensional water chains as extra-framework content. This feature may be found only in the synthetic Li-ABW and its Ga-analogous (Krogh Andersen & Ploug-Sørensen, 1986). Bikitaite has found an enormous interest in the industrial field as a candidate for the storage of nanophases in complex matrices. Moreover, this mineral is one of the few minerals containing Li, used as a strategic element in the electronic field, in particular in the production of energy accumulators.

The only two natural findings of bikitaite are related to pegmatitic genesis. The first one is the Bikita finding (Fort Victoria, Zimbabwe), characterized by a Li-rich pegmatite with spodumene, pethalite, lepidolite, eucryptite and quartz (Hurlbut, 1957). The second finding is localised in the King's Mountain area (North Carolina, USA). The phase

assemblage in these pegmatitic rocks is microcline, albite, quartz, spodumene, muscovite, rhodochrosite, eucryptite, as well as bikitaite (Leavens *et al.*, 1968).

The crystal framework of bikitaite is characterized by sheets of six-membered trydimite-like hexagonal rings of tetrahedra, linked by "pyroxene-type chains" (Gottardi & Galli, 1985) running along the b axis (Fig.1). The structure is characterized by two channel systems containing 8-membered rings (along the b axis) and 6-membered rings (along the c axis) (Fig. 1). Different samples of bikitaite show different Si, Al ordering on the tetrahedral centers, leading to different space groups. When there is partial disordering in the Si-Al distribution, the space group is $P2_1$ (Kocman *et al.*, 1974; Ståhl *et al.*, 1989), whereas complete ordering results in space group $P1$ (Bissert & Liebau, 1986; Quartieri *et al.*, 1999).

The extra-framework positions are occupied by (a) Li^+ cations, linked in four-fold coordination to three framework oxygens and one water oxygen and (b) water molecules linked by hydrogen bonds to form one-dimensional chains. No hydrogen-bond interactions were found

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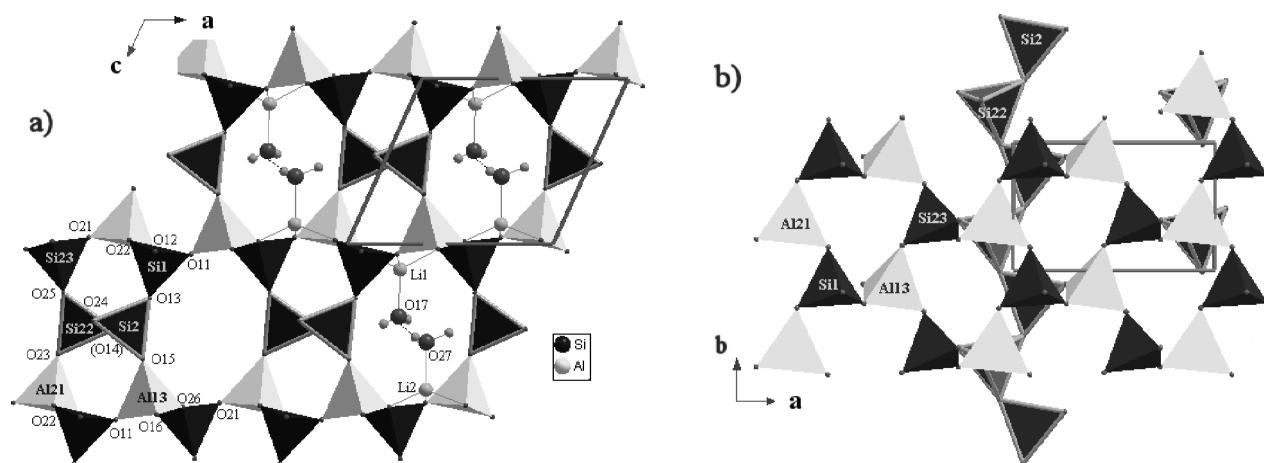


Fig. 1. Projection of bikitaite structure viewed perpendicular to the *ac* plane (a), showing the trydimite-like sheets, and perpendicular to the *ab* plane (b). The channel systems and the extraframework population are shown.

among the water molecules and the framework, as shown by Ståhl *et al.* (1989) using neutron diffraction data. The only interaction between the framework and the one-dimensional water chain is due to the Li cations. Fois *et al.* (1999) found that the water chain is stabilised by dipolar host/guest interactions between the dipolar water chain and the dipolar framework having opposite signs. The net polarization of the framework is probably due to the ditrigonal distortion of the hexagonal arrangement of tetrahedra on the *ab* plane.

The thermal stability of bikitaite was recently studied by Vezzalini *et al.* (2001) using synchrotron powder diffraction data. The authors showed that the water loss in bikitaite starts at 100°C and is completed at 450°C, the Li cations maintaining the original position in the channels. On the whole the bikitaite cell-volume undergoes very little variation, even at the temperature when complete dehydration occurs.

On the other hand, the baric behaviour of this very peculiar zeolite is almost unknown. Until now only preliminary data coming from *in situ* synchrotron X-ray powder diffraction have been collected by Vezzalini (2001). Our study intends to investigate the structural evolution of bikitaite under pressure by using *in situ* X-ray single-crystal

diffraction. An attempt to analyse the compressibility as a function of different non-penetrating pressure transmitting media was carried out, introducing glycerol or silicon-oil in the diamond anvil cell.

The knowledge of the behaviour of two other zeolites belonging to different groups, heulandite (Comodi *et al.*, 2001) and scolecite (Comodi *et al.*, 2002), allowed us to make a comparison of the baric behaviour and a tentative extrapolation to understand the general behaviour of zeolites under pressure.

Experimental method

The bikitaite specimen came from King's Mountain, North Carolina (USA). The sample and its chemical analysis were kindly supplied by S. Quartieri and G. Vezzalini. The chemical composition was determined at the "Dipartimento di Scienze della Terra" of Modena University with an ARL-SEMQ microprobe and the water content measured with thermogravimetric analysis, using a SEIKO SSC/5200 apparatus. The ideal crystal chemical formula $\text{Li}_2(\text{Al}_2\text{Si}_4\text{O}_{12}) \cdot 2\text{H}_2\text{O}$ was obtained, confirming Leavens *et al.*'s (1968) results.

Diffraction data were collected at room conditions on a Philips PW 1100 four-circle diffractometer using a graphite monochromator for $\text{MoK}\alpha$ radiation ($\lambda = 0.7107 \text{ \AA}$); and scans with scan width 1.8° and scan speed $0.10^\circ/\text{s}$ were used.

3362 independent reflections were measured in the range $3\text{--}40^\circ$. Data collection parameters are listed in Table 1. An empirical absorption correction based on the method of North *et al.* (1968) was applied. 2158 observed reflections with intensities higher than $4\sigma(I)$ were employed for the structural refinement (Table 1).

The refinement was carried out with anisotropic displacement parameters in space group *P1* using the SHELX-97 program (Sheldrick, 1997), starting from the atomic coordinates of Quartieri *et al.* (1999).

Table 1. Details of data collection and refinement of bikitaite.

Pressure (GPa)	0.0001	3.20	0.0001*
Radiation	$\text{MoK}\alpha$	$\text{MoK}\alpha$	$\text{MoK}\alpha$
θ -range ($^\circ$)	3–40	3–35	3–40
Scan type	ω	ω	ω
Scan speed ($^\circ/\text{s}$)	0.10	0.06	0.10
Scan width ($^\circ$)	1.8	2.6	1.8
Space Group	<i>P1</i>	<i>P1</i>	<i>P1</i>
No. Independent refl.	3362	829	3360
No. Observed refl.	2158	598	1973
No. Parameters	213	87	213
<i>R</i> (<i>F</i>) %	3.8	7.5	3.9

*data collected after decompression

Table 2a. Lattice parameters and volumes of bikitaite in glycerol at different pressures.

<i>P</i> (GPa)	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	α (°)	β (°)	γ (°)	<i>V</i> (Å ³)
0.0001	8.607(2)	4.956(2)	7.608(2)	89.92(5)	114.38(4)	89.83(3)	295.5(1)
0.55	8.582(3)	4.945(2)	7.588(2)	89.85(4)	114.45(5)	89.88(3)	293.1(2)
1.50	8.565(3)	4.916(2)	7.53(3)	89.77(4)	114.56(4)	90.03(4)	288.3(4)
2.15	8.551(4)	4.895(2)	7.472(5)	89.75(4)	114.62(4)	90.15(3)	284.3(5)
3.10	8.546(4)	4.858(3)	7.384(3)	89.67(5)	114.72(5)	90.32(4)	278.4(4)
3.20	8.543(5)	4.852(3)	7.377(3)	89.65(6)	114.74(5)	90.34(4)	277.7(4)
3.40	8.533(4)	4.842(3)	7.347(5)	89.59(5)	114.76(6)	90.38(5)	275.6(4)
4.15	8.523(5)	4.815(4)	7.309(5)	89.53(6)	114.80(5)	90.46(5)	272.2(5)
4.60	8.514(5)	4.805(5)	7.298(5)	89.47(6)	114.84(6)	90.48(7)	270.9(5)
4.80	8.507(6)	4.801(4)	7.269(6)	89.45(7)	114.86(6)	90.50(6)	269.3(5)
0.0001*	8.605(3)	4.957(2)	7.606(3)	89.93(4)	114.40(4)	89.85(3)	295.4(2)

*data collected after decompression

Table 2b. Lattice parameters and volumes of bikitaite in silicon-oil at different pressures.

<i>P</i> (GPa)	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	α (°)	β (°)	γ (°)	<i>V</i> (Å ³)
0.0001	8.607(2)	4.956(3)	7.601(2)	89.98(5)	114.38(3)	89.98(4)	295.3(2)
0.08	8.601(2)	4.954(3)	7.582(3)	89.97(5)	114.40(4)	89.99(5)	294.3(3)
0.38	8.570(4)	4.927(3)	7.573(2)	89.94(6)	114.53(3)	90.00(4)	290.9(3)
0.53	8.560(5)	4.915(5)	7.546(4)	89.89(5)	114.60(4)	90.05(5)	288.9(4)
0.83	8.545(5)	4.885(4)	7.473(5)	89.87(5)	114.71(4)	90.12(4)	283.4(4)
0.98	8.531(4)	4.876(6)	7.459(4)	89.86(6)	114.77(5)	90.27(5)	281.3(3)
1.24	8.525(5)	4.862(5)	7.421(5)	89.90(5)	114.81(6)	90.32(5)	279.2(4)
1.34	8.523(6)	4.851(5)	7.393(4)	89.92(6)	114.83(5)	90.39(6)	277.5(4)
1.65	8.511(5)	4.833(6)	7.353(5)	89.86(6)	114.86(5)	90.41(6)	274.4(5)
1.73	8.509(6)	4.824(6)	7.323(6)	89.88(6)	114.88(6)	90.42(5)	272.7(5)
1.88	8.510(7)	4.822(7)	7.280(6)	89.88(8)	114.91(6)	90.41(6)	271.3(5)
0.0001*	8.605(3)	4.955(3)	7.600(2)	89.95(5)	114.37(4)	89.97(4)	295.2(2)

* data collected after decompression

The final agreement index $R(F)$ was 3.8 % for 213 parameters. The neutral atomic scattering factor values from the *International Tables for X-ray Crystallography* (Ibers & Hamilton, 1974) were used.

A Merrill-Bassett diamond anvil cell (DAC) with 1/8 carat diamonds with 800 μm culet face diameter was used for the high-pressure study. A T301 steel foil, 250 μm thick, with a 300 μm hole, was used as gasket material. Ruby chips and a small crystal of quartz were used for pressure calibration as suggested by Angel *et al.* (1997). The fluorescence method (Mao *et al.*, 1986) was used to check the pressure by using ruby chips along with the diffractometric determination of the (101) interplanar distance of quartz (Angel *et al.*, 1997).

Glycerol, as non penetrating pressure-transmitting medium, was introduced into the DAC together with a sample having dimensions $0.130 \times 0.160 \times 0.06$ mm. The lattice parameters were measured at different pressures up to 4.8 GPa (Table 2a) by using the Bragg angles of 12–15 reflections accurately centered in the eight equivalent positions on the diffractometer (Angel *et al.*, 2000). Intensity data were collected at 3.2 GPa up to $\theta = 35^\circ$ adopting non-bisecting geometry (Denner *et al.*, 1978). Absorption by the pressure cell was corrected using an experimental attenuation curve (Finger & King, 1978). The structure was refined in space group $P1$. Due to the unfavourable obser-

vation/parameter ratio, individual isotropic atomic displacement parameters were used in refinement.

A further refinement was carried out on the same sample in air, after pressure release. The intensity data were measured with the same technique and parameters described above for the sample in air.

Details of data collection and structural refinements are given in Table 1, atomic positional and thermal parameters of all refinements are listed in Table 3; observed and calculated structure factors can be obtained from the authors upon request (or through the E.J.M. Editorial Office-Paris).

To analyse the role of the transmitting medium in the baric behaviour of bikitaite, another experiment was performed changing the transmitting medium. Silicon-oil was chosen because its large-sized molecules do not enter the zeolite framework channels. Moreover, even though its stability as a liquid phase was assured by Gillet *et al.* (1996) up to P greater than 15 GPa at room temperature, its real hydrostatic behaviour has recently been questioned by R. Angel (pers. comm.) even at pressure greater than 2 GPa.

A second sample with dimensions $0.14 \times 0.15 \times 0.06$ mm was mounted in the DAC with approximately the same orientation of the previous one. The lattice parameters were determined at different pressures up to 1.88 GPa using the method proposed by Comodi & Zanazzi (1993) (Table 2b). Significant peak broadening was observed at P

Table 3. Fractional atomic coordinates and thermal displacement factors ($\text{\AA}^2$).

Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} / <i>U</i> _{eq}
Li1	0.314(1)	0.366(2)	0.153(2)	0.016(2)
	0.297(5)	0.341(8)	0.167(17)	0.011(7)
	0.312(1)	0.363(2)	0.151(2)	0.022(2)
Li2	0.703(1)	0.868(2)	0.880(2)	0.019(2)
	0.677(5)	0.843(6)	0.833(15)	0.010(7)
	0.702(1)	0.866(2)	0.878(2)	0.022(2)
Si1	0.1070(2)	0.8641(3)	0.0995(2)	0.0079(2)
	0.104(1)	0.834(2)	0.105(4)	0.008(1)
	0.1072(2)	0.8644(3)	0.0990(2)	0.0093(2)
Si2	0.1038	0.8006	0.5049	0.0089(2)
	0.1038	0.8006	0.5049	0.012(1)
	0.1038	0.8006	0.5049	0.0099(2)
Si22	0.8924(2)	0.2995(4)	0.4881(2)	0.0094(2)
	0.892(1)	0.296(2)	0.496(3)	0.011(1)
	0.8925(2)	0.2991(3)	0.4880(2)	0.0101(2)
Si23	0.6196(2)	0.3747(3)	0.0650(2)	0.0079(2)
	0.616(1)	0.368(2)	0.073(4)	0.009(1)
	0.6197(2)	0.3747(3)	0.0648(2)	0.0084(2)
Al13	0.3805(2)	0.8743(4)	0.9393(3)	0.0086(2)
	0.377(1)	0.867(2)	0.942(4)	0.010(1)
	0.3808(2)	0.8745(4)	0.9391(3)	0.0084(2)
Al21	0.9004(2)	0.3643(4)	0.9089(3)	0.0091(2)
	0.898(1)	0.334(2)	0.934(5)	0.009(1)
	0.9003(2)	0.3647(4)	0.9086(3)	0.0095(2)
O11	0.2644(4)	0.7400(7)	0.0614(5)	0.0121(5)
	0.259(2)	0.713(3)	0.056(7)	0.014(3)
	0.2643(5)	0.7405(7)	0.0616(5)	0.0133(6)
O12	0.0863(4)	0.1822(7)	0.0454(5)	0.0128(6)
	0.089(2)	0.165(3)	0.074(7)	0.013(3)
	0.0864(5)	0.1824(7)	0.0456(5)	0.0132(6)
O13	0.1580(6)	0.8280(9)	0.3279(6)	0.0184(7)
	0.157(2)	0.746(4)	0.327(8)	0.017(4)
	0.1599(6)	0.8286(9)	0.3287(6)	0.0196(7)
O14	0.0542(5)	0.4865(8)	0.5145(7)	0.0196(7)
	0.056(2)	0.514(3)	0.581(6)	0.011(3)
	0.0553(5)	0.4858(8)	0.5144(7)	0.0212(8)
O15	0.2606(5)	0.8916(8)	0.6949(6)	0.0182(7)
	0.263(2)	0.947(4)	0.703(7)	0.013(3)
	0.2612(6)	0.8924(9)	0.6956(6)	0.0196(7)
O16	0.4523(4)	0.1969(7)	0.0305(5)	0.0120(5)
	0.460(2)	0.178(3)	0.074(7)	0.011(3)
	0.4524(5)	0.1965(7)	0.0311(5)	0.0127(6)
O17	0.4100(7)	0.325(1)	0.4377(8)	0.0290(9)
	0.414(2)	0.286(4)	0.473(7)	0.022(4)
	0.4089(8)	0.325(1)	0.4391(9)	0.031(1)
O21	0.7311(4)	0.2426(7)	0.9592(5)	0.0117(5)
	0.720(2)	0.217(3)	0.966(6)	0.015(3)
	0.7316(4)	0.2447(7)	0.9588(5)	0.0122(5)
O22	0.9315(4)	0.7054(7)	0.9751(5)	0.0132(6)
	0.923(2)	0.680(3)	0.967(7)	0.009(3)
	0.9313(5)	0.7050(7)	0.9758(6)	0.0144(6)
O23	0.8408(6)	0.3284(9)	0.6648(6)	0.0214(8)
	0.831(3)	0.249(4)	0.670(9)	0.009(3)
	0.8422(6)	0.3278(9)	0.6656(6)	0.0208(8)
O24	0.9368(5)	0.9863(7)	0.4637(6)	0.0188(7)
	0.935(2)	1.011(4)	0.420(8)	0.023(4)
	0.9370(5)	0.9879(8)	0.4644(7)	0.0202(7)
O25	0.7321(5)	0.3933(8)	0.2968(5)	0.0176(7)
	0.739(2)	0.433(4)	0.306(7)	0.012(3)
	0.7317(5)	0.3925(9)	0.2968(6)	0.0187(7)
O26	0.5621(4)	0.6772(7)	0.9838(5)	0.0121(5)
	0.543(2)	0.654(3)	0.952(7)	0.009(3)
	0.5617(5)	0.6785(7)	0.9847(5)	0.0129(6)
O27	0.6008(7)	0.822(1)	0.5924(8)	0.031(1)
	0.585(3)	0.779(4)	0.551(9)	0.031(5)
	0.6010(7)	0.822(1)	0.5921(8)	0.032(1)
H11	0.352(9)	0.30(1)	0.48(1)	0.01(1)
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	0.33(1)	0.34(2)	0.48(1)	0.04(3)
H12	0.46(1)	0.19(2)	0.46(1)	0.04(3)
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	0.45(1)	0.23(2)	0.45(1)	0.01(2)
H21	0.69(2)	0.85(3)	0.53(3)	0.14(7)
	--	--	--	--
	0.68(3)	0.80(4)	0.56(3)	0.13(7)
H22	0.54(1)	0.72(2)	0.56(1)	0.04(2)
	--	--	--	--
	0.56(2)	0.65(3)	0.74(2)	0.08(4)

Note: The uppermost values refer to the room condition refinement, the intermediate values refer to refinement at 3.2 GPa and the lowest ones to the refinement at room condition after decompression. For *HP* refinement isothermal thermal parameters (*U*_{iso}) are reported, whereas for room condition refinements the anisotropic thermal parameters are reported as *U*_{eq}. H positions were not determined in the *HP* refinement.

higher than 1.8 GPa. At 2.0 GPa the peak broadening hindered the determination of the lattice parameters.

Results

Structure results at ambient conditions

The structural refinement perfectly agreed with that obtained by Bissert & Liebau (1986) for the bikitaite from Bikita (Zimbabwe) and with that obtained by Quartieri *et al.* (1999) for the bikitaite from North Carolina (USA).

The complete ordering of Si-Al on the tetrahedral sites was confirmed by the tetrahedral bond distances (Table 4), which were in the range 1.609–1.621 Å and 1.743–1.746 Å, respectively.

No interaction between the water molecules of the chain and the oxygens of the framework emerged from the pertaining interatomic distances.

Compressibility

Figure 2a and Table 2a report the evolution of the lattice parameters with pressure when the sample was compressed by using glycerol as non-penetrating pressure-transmitting medium. All lattice parameters decreased linearly in the pressure range investigated. A strong anisotropic compression was observed by linear regressions, bikitaite being softer along the *c* axis ($\beta_c = 9.3(1) \cdot 10^{-3} \text{ GPa}^{-1}$), than along *b* ($\beta_b = 6.6(1) \cdot 10^{-3} \text{ GPa}^{-1}$) and *a* ($\beta_a = 2.4(1) \cdot 10^{-3} \text{ GPa}^{-1}$). Similar results may be obtained by calculating the compressibility coefficients with a second order “linearized” Birch-Murnaghan equation of state (Angel, 2000), by using the Downs’ software (Downs, 1994). The axial compressibility values were: $\beta_a = 2.56(1) \cdot 10^{-3}$, $\beta_b = 8.4(1) \cdot 10^{-3}$, $\beta_c = 1.20(2) \cdot 10^{-2} \text{ GPa}^{-1}$ ($\beta_a : \beta_b : \beta_c = 1 : 3.28 : 4.69$). Absence of significant distortion in the

Table 4. Interatomic distances (Å) as a function of pressure.

P (GPa)	0.0001	3.20	0.0001*
Li1-O11	1.964(10)	1.947(41)	1.973(11)
Li1-O12	2.002(10)	1.825(48)	1.987(12)
Li1-O16	1.976(10)	1.959(72)	1.967(12)
Li1-O17	1.983(12)	2.072(90)	2.007(14)
<Li1-O>	1.981	1.951	1.983
Li2-O21	1.938(10)	2.026(71)	1.958(12)
Li2-O22	1.966(10)	2.069(36)	1.969(11)
Li2-O26	1.941(12)	1.930(56)	1.943(10)
Li2-O27	2.005(12)	1.913(90)	1.997(14)
<Li2-O>	1.962	1.984	1.967
Si1-O11	1.619(3)	1.621(23)	1.612(4)
Si1-O12	1.620(4)	1.617(14)	1.618(4)
Si1-O13	1.615(4)	1.563(49)	1.623(4)
Si1-O22	1.618(3)	1.633(27)	1.622(4)
<Si1-O>	1.618	1.608	1.619
Si2-O13	1.601(4)	1.582(47)	1.607(4)
Si2-O14	1.624(4)	1.610(16)	1.625(4)
Si2-O15	1.582(4)	1.684(42)	1.590(4)
Si2-O24	1.624(4)	1.664(15)	1.626(4)
<Si2-O>	1.608	1.635	1.612
Si22-O14	1.615(4)	1.652(19)	1.623(4)
Si22-O23	1.586(4)	1.594(47)	1.586(4)
Si22-O24	1.628(4)	1.590(34)	1.617(4)
Si22-O25	1.605(4)	1.606(31)	1.605(4)
<Si22-O>	1.608	1.610	1.608
Si23-O16	1.615(3)	1.624(13)	1.619(4)
Si23-O21	1.623(3)	1.595(32)	1.622(4)
Si23-O25	1.625(4)	1.630(49)	1.626(4)
Si23-O26	1.618(4)	1.625(17)	1.622(4)
<Si23-O>	1.620	1.618	1.622
Al13-O11	1.751(4)	1.726(25)	1.757(4)
Al13-O15	1.715(4)	1.664(49)	1.709(4)
Al13-O16	1.751(4)	1.777(30)	1.752(4)
Al13-O26	1.753(4)	1.738(17)	1.742(4)
<Al13-O>	1.742	1.726	1.740
Al21-O12	1.755(4)	1.730(19)	1.754(4)
Al21-O21	1.759(3)	1.722(18)	1.752(4)
Al21-O22	1.753(4)	1.701(20)	1.752(4)
Al21-O23	1.717(4)	1.837(49)	1.714(4)
<Al21-O>	1.746	1.747	1.743

* data collected after decompression.

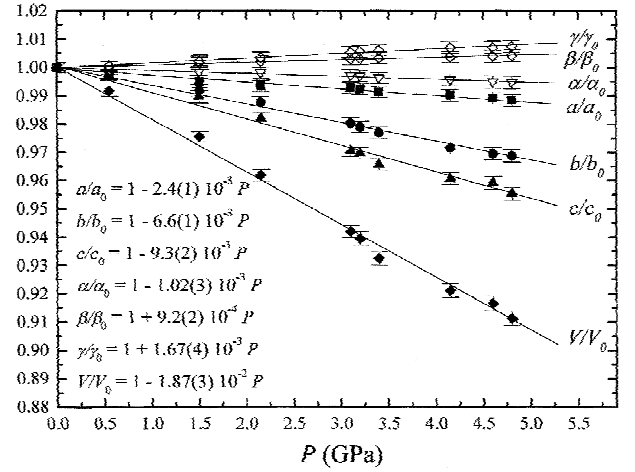


Fig. 2a. Unit-cell parameters of bikitaite in glycerol, normalised to room condition value, vs. pressure. The regression line equations are reported in the bottom left-hand corner.

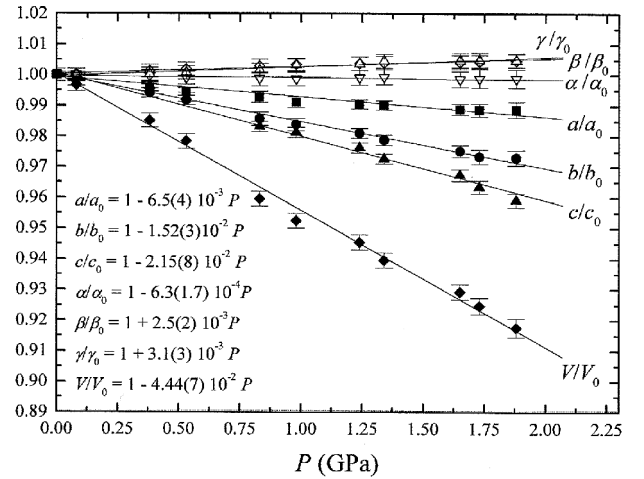


Fig. 2b. Unit-cell parameters of bikitaite in silicon-oil, normalised to room condition value, vs. pressure. The regression line equations are reported in the bottom left-hand corner.

unit-cell is verified by the small changes in the α , β , γ angles; in particular the β and γ angles increased slightly with pressure ($9.2(2) \cdot 10^{-4}$ and $1.67(4) \cdot 10^{-3}$ deg. GPa $^{-1}$, respectively) whereas the α angle decreased slightly ($-1.02(3) \cdot 10^{-3}$ deg. GPa $^{-1}$).

Because the triclinic symmetry does not constrain the principal strain vectors to coincide with the lattice parameters, the orientation of the strain ellipsoid was calculated with the program STRAIN (Ohashi, 1982) (Fig. 3). The principal strain tensor components, determined from the lattice parameters obtained from the linear regression calculation between 1.0 and 3.0 GPa, are reported in Table 5.

Cell volumes at different pressures were transformed into finite strain (f) and “normalized stress” (F_e) (Angel, 2000) and plotted (Fig. 4) to obtain a direct indication of the compressional behaviour. This plot shows a linear and almost horizontal trend, indicating that there are no phase transitions and that the volume data can be fitted using a second order

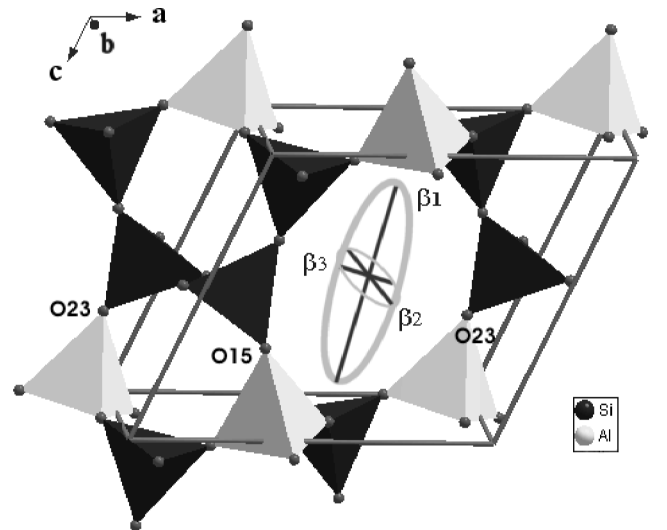


Fig. 3. Strain ellipsoid orientation of bikitaite in glycerol.

Table 5. Strain tensor components of bikitaite in glycerol and silicon-oil.

Pressure medium	glycerol			silicon-oil		
Pressure range (GPa)	1.0 – 3.0			0 – 1.5		
Main axes of the strain ellipsoid (GPa ⁻¹)	β_1	β_2	β_3	β_1	β_2	β_3
	$1.07(5) \cdot 10^{-2}$	$7.2(4) \cdot 10^{-3}$	$1.7(5) \cdot 10^{-3}$	$2.4(5) \cdot 10^{-2}$	$1.57(7) \cdot 10^{-2}$	$5.9(5) \cdot 10^{-3}$
Orientation (°)						
$\beta_n \wedge a$	96±3	77±2	14±2	92±2	75±3	14±3
$\beta_n \wedge b$	96±3	15±2	103 ±3	84±4	15±4	104 ±3
$\beta_n \wedge c$	19±2	89±3	108±2	22±3	101±2	109±2

Birch-Murnaghan equation of state. The fit yielded $K_0 = 44.2(4)$ GPa, with $K' = 4$ and $V_0 = 295.58(2)$ Å³, coincident with the value measured at room conditions.

This value of K_0 is intermediate between the values measured for heulandite and scolecite, where K_0 values were 27.5(2) GPa (Comodi *et al.*, 2001) and 54.6(3) GPa (Comodi *et al.*, 2002) respectively.

When the silicon-oil was used as non penetrating pressure-transmitting medium the compressibility of bikitaite was remarkably different compared to the compressibility with glycerol (Fig. 2b). The lattice parameter compressibilities obtained from the linear regression of the data collected at different pressures up to 1.8 GPa were: $\beta_a = 6.5(4) \cdot 10^{-3}$, $\beta_b = 1.52(3) \cdot 10^{-2}$, $\beta_c = 2.15(8) \cdot 10^{-2}$ GPa⁻¹.

The principal strains obtained with the same procedure as mentioned above were: $\beta_1 = 2.4(5) \cdot 10^{-2}$, $\beta_2 = 1.57(7) \cdot 10^{-2}$, $\beta_3 = 5.9(5) \cdot 10^{-3}$ GPa⁻¹. Their orientation compared to the crystallographic axes is given in Table 5.

On the whole the orientation of the strain ellipsoids and the ratio between the principal axes were very similar using glycerol or silicon-oil as non penetrating pressure media, but the absolute values of the principal axes were larger when silicon-oil was introduced in the diamond anvil cell. This result may be highlighted when a second order Birch-Murnaghan equation of state is used to determine the bulk modulus. A bulk modulus of 18.8 (4) GPa,

$K' = 4$ and $V_0 = 295.3(1)$ Å³ are obtained. K_0 is about half of the bulk modulus measured with glycerol. In order to compare the results the evolution of the cell volume with pressure for the two different media is shown in Fig. 5. By comparing the two data sets with those of Vezzalini (2001), obtained by *in situ* synchrotron X-ray powder diffraction, we observe a better agreement with the data obtained using glycerol than those obtained using silicon-oil.

The pressure ranges investigated were also very different when using the two pressure media: in fact with glycerol lattice parameters were measured up to about 5.0 GPa, while with silicon-oil the pressure range was limited up to 1.8 GPa. In both cases the highest pressure limit achieved was conditioned by the broadening of reflections which hindered correct lattice parameter measurements. In any case the process was completely reversible and the crystal was maintained after decompression (results from structure refinement after decompression are listed in Tables 1, 2a, 2b, 3, 4, 6).

Structural features at 3.2 GPa

Structural evolution of bikitaite with pressure was studied by comparing the data collected under room conditions and at 3.2 GPa when glycerol was used in the DAC.

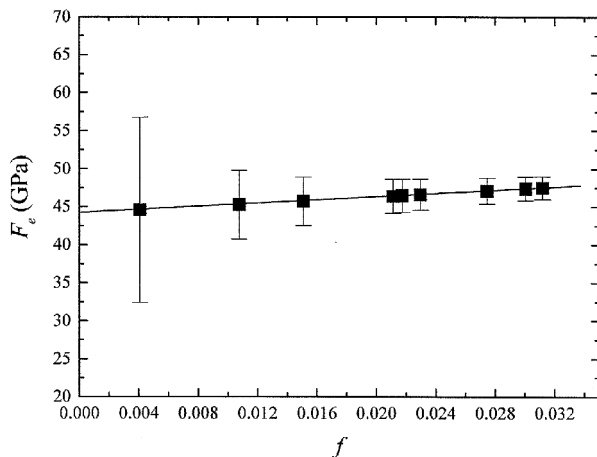


Fig. 4. Plot of the “normalised stress”, defined as $F_e = P/[3f(1+2f)^{5/2}]$, vs. the finite strain $f = [(V_0/V)^{2/3} - 1]/2$ for bikitaite in glycerol. The e.s.d.s were calculated according to Heinz & Jeanloz (1984).

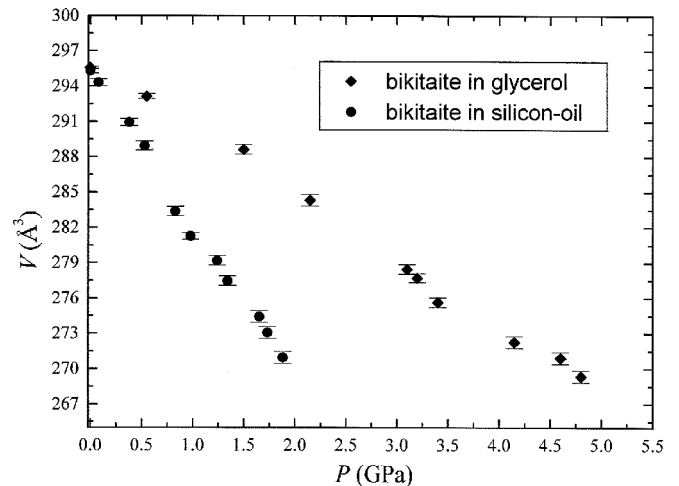


Fig. 5. Cell volume of bikitaite vs. pressure in glycerol and silicon-oil.

Table 6. Relevant structural parameters in bikitaite at different pressures. The O...O distances refer to the free diameters in the channels.

<i>P</i> (GPa)	0.0001	3.20	0.0001*	<i>K</i> (GPa)	
[010] Channel					
8-ring channel					
O11-O21(Å)	4.092(4)	3.945(7)	4.083(2)	13.3(1.1)	
O15-O23(Å)	3.106(3)	3.319(4)	3.111(4)		
O13-O25(Å)	2.784(4)	2.565(5)	2.776(4)		
O26-O26(Å)	4.901(4)	4.677(8)	4.906(6)		
V _{ch} 8-ring (Å ³)	58.3(3)	52.4(5)	58.1(3)		
O17-O27 (Å)	2.950(4)	2.798(6)	2.948(5)		
O27-O17 (Å)	2.923(3)	2.732(5)	2.931(4)		
O27-O27 (Å)	4.956(5)	4.852(6)	4.957(5)		
O27-O17-O27(°)	115.0(2)	122.6(4)	114.9(2)		
5-ring (up) channel					
O25-O13(Å)	1.474(5)	1.120(6)	1.497(5)	10.0(2.0)	
O13-O21(Å)	1.913(4)	1.689(7)	1.924(5)		
O22-O14(Å)	1.240(6)	1.552(6)	1.234(4)		
V _{ch} 5-ring (up)(Å ³)	17.7(3)	15.2(5)	17.7(4)		
5-ring (down) channel					
O15-O23(Å)	1.797(4)	2.232(7)	1.801(4)		10.7(1.6)
O15-O22(Å)	1.589(3)	1.614(6)	1.597(4)		
O14-O11(Å)	1.291(4)	0.643(8)	1.298(3)		
V _{ch} 5-ring (down)(Å ³)	18.5(1)	16.1(4)	18.4(3)		
Si1-O13-Si2(°)	150.2(2)	139.6(3)	149.3(3)	15.1(2.2)	
Si2-O15-Al13(°)	151.6(3)	136.3(5)	151.5(4)		
Al21-O23-Si22(°)	149.4(2)	139.7(4)	150.1(4)		
Si22-O25-Si23(°)	150.5(3)	139.9(5)	150.3(2)		
Si23-O26-Al13(°)	134.1(5)	130.7(7)	134.5(6)		
Si23-O21-Al21(°)	132.9(3)	128.4(6)	133.4(5)		
Al13-O11-Si1(°)	130.7(3)	130.3(5)	130.8(3)		
Si22-O14-Si2(°)	140.7(2)	135.7(5)	140.2(4)		
Si1-O22-Al21(°)	129.2(4)	124.6(7)	129.3(6)		
O24-O14-O24(°)	139.2(4)	127.3(7)	138.9(5)		
[001] Channel					
6-ring channel					
O11-O11(Å)	2.256(3)	2.152(6)	2.257(4)		15.1(2.2)
O12-O16(Å)	0.500(2)	0.466(4)	0.498(4)		
O22-O16(Å)	2.306(3)	2.286(6)	2.302(4)		
O12-O26(Å)	2.260(3)	2.229(5)	2.260(3)		
O16-O11(Å)	0.498(4)	0.391(8)	0.499(5)		
O11-O12(Å)	0.440(3)	0.349(6)	0.443(2)		
V _{ch} 6-ring (Å ³)	39.4(3)	35.8(6)	39.2(3)		

* data collected after decompression

As observed in many silicates in this pressure range, the tetrahedra behaved as rigid units. Their bond lengths and volumes remained nearly unchanged, but changed their orientation, through the well known mechanism of “polyhedral tilting” (Hazen & Finger, 1982).

Zeolite structures and their characteristic structural feature with large channels and a framework with rigid but very flexible units can represent one of the best examples of polyhedral tilting. Data from single-crystal experiments are fundamental to understand the principal deformation mechanisms which are different for every zeolite type.

In the case of bikitaite, the comparison of structural refinements under room pressure and at high pressure

showed that the compressibility of the three channels did not show relevant differences. In fact, when the bulk moduli of the channels were calculated through the volume changes of the cylinders inscribed inside the channels, very similar values were observed. The bulk modulus K_0 was calculated as $K_0 = \beta^{-1} = -V(\partial P/\partial V)_T$. The bulk moduli of 8-ring and 6-ring channels were respectively 13.3(1.1) and 15.1(2.2) GPa (Table 6).

The other two systems of 5-ring channels running along [010], here defined as “5-ring up” (Si23-Al21-Si1-Si2-Si22, Fig. 1) and “5-ring down” (Si22-Si2-Al13-Si1-Al21, Fig. 1), showed greater compressibility than the former two: the bulk moduli were 10.0(2.0) and 10.7(1.6) GPa, respectively (Table 6).

Concerning the evolution of the single interatomic distances, the channels behaved in a very different way. The principal deformation mechanism is especially reflected in the 5-ring channels. In the pyroxene-like chains (.....O24-Si2-O14-Si22-O24....), the kinking increased with pressure (the O24-O14-O24 angle changed from $139.2(4)^\circ$ at 0.0001 GPa to $127.3(7)^\circ$ at 3.2 GPa, Table 6), pushing the O14 oxygen toward the center of the 5-ring-down. The free diameter O14-O11 changed from 1.291(4) Å at room condition to 0.643 (6) Å at 3.2 GPa (Table 6). This O4 shift is responsible for the increase of the O22-O14 free diameter in the 5 ring-up channel, which increased from 1.240(6) Å at room condition to 1.552(6) Å at 3.2 GPa (Table 6).

The 8-ring channel along [010] and the 6-ring channel along [001] did not show relevant variations in their shapes with *P*: they decreased in size, but maintained the same degree of ellipticity as observed at room condition.

The structural refinement allowed us to understand the strong anisotropy observed in the lattice parameter compressibilities. The main deformation mechanism, represented by the shortening of the O14-O11 distance, justifies a strong compressibility of the *c* axis since the angle between the vector O14-O11 and *c* is about $15\text{--}20^\circ$. On the other hand the *a* axis was the least compressible. In fact along this direction, in contrast with the general decrease, an increase of the size of the 5-ring and 8-ring channels was observed, as shown by the O23-O15 and O15-O23 distances (Fig. 3, Table 6).

The compressibility of *b* axis was intermediate between those of *a* and *c* axes, related to the pyroxene-like chain kinking.

The Li positions and those of the water molecules did not change with *P*. The water chain presented small changes in form and dimension with pressure increase but no interaction with framework was established. The distances between the oxygens decreased: the O27-O27 distance changed from 4.956(5) to 4.852(6) Å, whereas the O27-O17-O27 angle increased from $115.0(2)$ to $122.6(4)^\circ$ (Table 6). There were two combined effects: one was the shortening of the oxygen-oxygen distances, to allocate the compression along [010], and the second one was the stretching of the chain due to the increase of the O27-O17-O27 angle, to allocate the compression in the plane perpendicular to [010]. On the whole there was a reduction in the chain length along the [010] direction, namely in the O27-O27 distance.

The low quality of high pressure refinement hindered the proton positions to be determined, and the direct analysis of the interaction between the water chain and the framework. Anyway the O...O distances between chain oxygens and framework oxygens always remained higher than 3 Å, ruling out a possible interaction between the two structural units.

Discussion and conclusions

So far we have collected information on the structural effect of high pressure on three zeolites, namely bikitaite,

heulandite (Comodi *et al.*, 2001) and scolecite (Comodi *et al.*, 2002) and we can extrapolate some general considerations.

1) We have shown that the compressibility is not directly related to the micro-porosity represented by the framework density (FD, Meier *et al.*, 1996). In fact the bulk moduli of heulandite and scolecite are different even though their FD's are quite similar ($FD_{\text{heul}} = 17.0 \text{ T/1000 } \text{\AA}^3$, $K_{0\text{heul}} = 27.5 \text{ GPa}$; $FD_{\text{scol}} = 17.8 \text{ T/1000 } \text{\AA}^3$, $K_{0\text{scol}} = 54.6 \text{ GPa}$; $FD_{\text{bikit}} = 20.2 \text{ T/1000 } \text{\AA}^3$, $K_{0\text{bikit}} = 44.2 \text{ GPa}$).

2) The structural behaviour using non penetrating media is strongly controlled by the framework and the role of the extra-framework contents is secondary in all three zeolites. In fact in bikitaite the Li positions remain unchanged with pressure and no interaction between the framework and water chain is induced by the pressure increase. Very similar behaviour was observed in heulandite and scolecite, where the extra-framework cations and water molecules remain in the same position measured under room conditions even at high pressure. The extra-framework cation did not increase their coordination number and no new hydrogen bridges were generated in the pressure range investigated.

3) On the other hand, the role of the extra-framework population in the thermal behaviour of these three zeolites was very different. In fact, upon the complete dehydration process, the bikitaite cell volume underwent variation smaller than 1 % (Vezzalini *et al.*, 2001). In heulandite the dehydration process determined a sharp change in the cell volume, about 16 % (Alberti & Vezzalini, 1983), and in scolecite the loss of the water molecule induced a phase transition from *F1d1* to *Fd11* (Stahl & Hanson, 1994) and a rearrangement of the Ca-water coordination.

4) Bikitaite experiments, carried out both with glycerol and silicon-oil, indicated at first approximation, a strong control of pressure media on the compressibility, even if both of them were non-penetrating. Actually the compressibility measured by using glycerol or silicon-oil was very different (Fig. 5) as was the investigable pressure range, due to diffraction peak enlargements: 1.8 GPa with silicon-oil and 4.8 GPa with glycerol. The peak enlargements were reversible when the diffraction data were re-measured at room condition after decompression, by using both pressure media, clear indication of incoming elastic strain (Downs *et al.*, 1996). The hydrostaticity of glycerol is well tested up to 4 GPa (Hazen & Finger, 1984), and for mixture glycerol-water 3:2, up to 5 GPa (Sidorov & Tsiok, 1991), but for silicon-oil there are some conflicting results and recently R. Angel (pers. comm.) has questioned its real hydrostaticity, even at low pressure, lower than 2 GPa.

We believe that the different results we obtained for bikitaite in silicon-oil and in glycerol might be associated with the non-hydrostaticity of the pressure transmitting medium, which in the case of a strongly anisotropic structure, like bikitaite, might produce dramatic effects even on the compressibility pattern, when using data from single-crystal experiments. On the contrary, in powder diffraction experiments, this phenomenon might be reduced, in part or completely, because of the random orientation of the crys-

tallites, which could mediate differential effects of the deviatoric stress in the cell.

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